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Decontamination of Casualties from Battlefield
Under CW and BW Attack

FINAL REPORT

Robert E. Lyle, Ph.D.
Henry F. Hamil, Ph.D.
Edward P. McGovern, Ph.D.
David A. Trujillo, Ph.D.

November 15, 1984

U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701-5012

Contract No. DAMD17-83-C-3128

Southwest Research Institute
6220 Culebra Road
P.O. Drawer 28510
San Antonio, TX 78284

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06	17		
07	03		

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

A series of activated clays were evaluated for their ability to adsorb and/or react with simulants of mustard (HD). The simulant was chloroethylethylsulfide (CEES). Using the newly developed "washer test" for total adsorption-decomposition, the clay sample was considerably more effective in stopping CEES than was Fuller's Earth. A measured decomposition rate of 4 minutes for the simulant CEES showed the clays to be much better than Fuller's Earth or samples of proprietary polymers. The results with the simulant diethyl chlorophosphate (DECP) were not clear-cut, since certain clay samples appeared to encapsulate the agent without destroying it. Attempts to identify products of the decomposition were only partly successful, since the products seemed to be bound to clay. Hydrolysis products of the DECP were detected.

Reactive monomers of vinyl benzyl chloride were grafted onto polyethylene films and converted to quaternary salts. The anion of these salts was exchanged to give highly nucleo-

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philic hydroxide, azide, or thiosulfate salts. Oxidative anions such as permanganate
chromate, perchlorate, chlorate, or hypochloride were also formed. These films had
low capacity for decontamination but could be treated with indicators to form
detection films.

Polymers having the diethylene triamine side chain were prepared. Attempts to
prepare a polymeric form of DS-2 (a sodium hydroxide-containing decontaminant) were
interrupted by the close of the project.

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FOREWORD

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I. INTRODUCTION AND BACKGROUND

The treatment of wound casualties on a battlefield in which chemical and/or biological agents are being used is complicated for both the casualty and the medical team that is supplying aid. In order to provide the optimum conditions for treatment of wounds in this situation, it is essential that a method be devised to protect and decontaminate and contain any chemical agent remaining on the casulty or his clothing. In most instances the casualty will be clothed in an ensemble for protection against agent exposure, but this protective barrier will be compromised by the munition which caused the wound. Thus it is desirable that the treatment also seal the ensemble to prevent further exposure of the casualty to chemical agents.

Determining the method of treatment is further complicated because the decontaminating agent must be sufficiently mild that it will not cause significant damage to the exposed skin. In general, this would eliminate strong caustic solutions, such as DS-2, or the highly potent oxidizing agents, such as (super tropical bleach (STB). It is presumed, therefore, that a more satisfactory approach to reactive decontamination would be the use of the milder oxidizing agents, such as soft halogens, or weaker nucleophilic reagents, such as amines.

The approach proposed by SwRI to meet these criteria is twofold. Consideration of the procedure of the Canadian and British Air Forces [1] to decontaminate with Fuller's Earth suggested the possibility of utilizing a packet or bandage of porous cloth containing a reactive adsorbent, such as a clay, with a reactive surface coating. This packet would allow the chemical agent to enter by diffusion for adsorption and reaction with the clay. The second approach utilizes a reactive film, which could be used as a covering or perhaps as a thread in a woven bandage. Either of these could be placed over the wound to provide protection against further entry of chemical agents, to provide decomposition of any agent in the vicinity of the entry point, and detoxification of any chemical or biological agent on the ensemble for the protection of the medical team treating the casualty.

A. Reactive, Adsorbent Clays

A currently available activated clay has been under investigation as a surface for other reactive functions. Anglo-American Clays of Sandersville, Georgia, has used a proprietary process to introduce highly adsorbent or reactive surfaces on a treated bentonite clay. Prior to this contract several samples of these clays had been examined for their effectiveness in reducing the vapor pressure of benzyl bromide, which was used as a simulant

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for mustard (HD).[2] The effectiveness of the treated clays for reducing the vapor pressure of benzyl bromide was approximately one order of magnitude greater than that of a comparable weight of Fuller's Earth.

The proprietary method used by Anglo-American Clays for introducing reactive surfaces on the clay also could be used to introduce a nucleophilic amine, such as ethylene diamine or diethylene triamine (DETA), on the surface of this clay. They have methods for increasing the surface area of the clay creating large pore sizes, and allowing intercalation of catalytic metal ions in the layers of the clay. Thus the action of the treated clay would be twofold: (1) The adsorption would reduce the vapor pressure of the chemical agent surrounding the wound, and (2) the reactive surface would irreversibly deactivate the chemical or biological agent near the wound by a slower mechanism. The proprietary methods of clay treatment used by Anglo-American Clays were not disclosed to SwRI. The properties desired for the clays were determined by conference between SwRI and Anglo-American Clays and then were furnished by the latter on issue of a purchase order for the sample.

B.   Reactive Grafted Polymer Films

The Polymer Chemistry Section of the Chemistry and Chemical Engineering Division of Southwest Research Institute has shown the effectiveness of grafting polymers by utilizing an ionizing radiation soruce to induce the polymerizaticn. By this technique, reactive surfaces have been introduced on a variety of inert films such as polyethylene, Teflon, and similar paraffins.[3]

Utilizing this technique, polyvinyl pyridines have been grafted to polyethylene. The pyridine nucleus of these films was then treated with an alkylating agent such as methyl iodide and the halide ion converted to a variety of reactive polyatomic anions such as I_3^-, Br_3^-, and N_3^-. The perhalide forms of grafted films are the subject of a patent disclosure and must be considered proprietary.

The films have several interesting properties. (1) As one might expect, the trihalide foim of the quaternary salt has a highly intense color, and as the film undergoes reaction with reduction of the trihalide ion, the color fades. Thus the film acts as an indicator showing when the reactivity of the film has been expended. (2) A family of perhalides and mixed halogen salts could be prepared from these grafted vinyl pyridine polymer films. Thus a range of oxidizing activities could be obtained to balance the reactivity required for the deactivation of chemical and biological agents with the mildness required for compatibility with human skin. (3) The preliminary

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studies show that the film can be regenerated to the perhalide form by washing the film with a halogen solution in chloroform or the trihalide solution in water. Because their properties seemed suitable, the films were studied for their use in decontamination or detection systems.

The objectives of this project were:

- Design and procure the decontamination materials

- Select simulants for the chemical agents

- Develop analytical methods for evaluating the decontamination materials

- Introduce a color detector system into the decontamination material

II. EXPERIMENTAL METHODS

The simulants used are given in Table I and were obtained from Aldrich Chemical Co. The clays are given in Table II and were obtained from Anglo-American Clays Corporation.

A. Evaluation of Clays with Nerve and Mustard Simulants Using Headspace Analysis

A series of 200 mg samples of clay, as received from Anglo-American Clays or modified by methanolic Na⁺ treatment, were placed in 4 mL septum-sealed vials. Using a Hamilton syringe, 10, 20, 40 or 60 µL of the simulant was injected directly into the clay and the vial was immediately placed in a vortex mixer for 1 minute. A 20 µL sample of vapor from the headspace above the clay was withdrawn with a 50 µL gas-tight syringe and analyzed by gas chromatography (GC). The vapor height for the simulant was compared to that for a sample from pure simulant with no clay added, about 200 mm. The results for clays A'-E' are given in Figures 1, 2 and 3. The data for clays 1-5 were plotted as a percentage of the peak height of the standard with no clay added. These results are given in Figures 4 and 5.

B. Evaluation of Clays by Extraction

As in the headspace method, 40 µL of simulant was added to 200 mg, of clay, which was stirred on a vortex mixer for 1 minute and then allowed to stand for 5 additional minutes. At this time 2 mL of ether was added; a 1:100 dilution of the ether solution was analyzed by gas chromatography using an alkali flame ionization detector (GC-AFID). A solution of untreated simulant (no clay) was the standard. The results for clays 1-6, as percentage of recovered simulant, are presented in Figures 6 and 7.

C. Procedure for Comparing Reactivities of Clays with CEES

1. Method 1

A 200 mg sample of clay was weighed into a vial and 40 µL of chloroethyl ethyl sulfide CEES was added. The sample was mixed on a vortex mixer for 1 minute. After standing for 5 minutes, the sample was extracted with 2 mL of. diethyl ether and the extract was analyzed by GC-AFID.

2. Method 2

The procedure of Method 1 was followed, except that only 20 µL of chloroethyl ethyl sulfide (CEES) was added and the mixture was allowed to stand 15 minutes before extraction.

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TABLE I
SIMULANTS FOR CHEMICAL AGENTS

Simulant	Structure	Abbreviation	Agent Simulant	Type
Chloroethyl ethyl Sulfide	$ClCH_2CH_2SCH_2CH_3$	CEES	HD	Blister Agent
Diethylsulfide	$CH_3CH_2SCH_2CH_3$	DES	HD	Blister Agent
Diethyl chloro-Phosphate	$(C_2H_5O)_2POCl$	DECP	GB	Nerve Agent
O-Ethyl-S-ethyl Methylphosphoro-thioate	C_2H_5O C_2H_5S PCH_3	EEMPT	VX	Nerve Agent

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TABLE II

CONTROL CLAYS AND MODIFICATIONS RECEIVED
FROM ANGLO-AMERICAN CLAYS CORPORATION

Identifying Symbol	Treatment
A'	Control clay Irwin
B'	Control clay sodium bentonite
C'	1% Diethylene triamine (DETA) on A'
D'	1% DETA on B'
E'	10% DETA on B'
1	Surfaced bonded ammonia
2 or 4374	Intercalated ethylene diamine (EDA)
4375T	Surface bonded EDA
3	Surface bonded urea
4	DETA different from C', D', or E'
5	Variation of 4
6	Control clay for samples 1-5
RT001	Acid activated
RT002	Variation of RT001
RT003	Beneficiated clay
RT004	Beneficiated clay, calcined at 250°, 60 m^2/g surface area
RT005	Al^{+3}/Cr^{+3} intercalated
RT006	Cr^{+3} intercalated
RT007	High surface area, 400 m^2/g, pore size of 12-14 Å
RT008	Cu^{+2} intercalated
RT009	Cr^{+3} intercalated, 180-200 m^2/g surface area
4952	Acid wash, dried
4953	Surface acidified
4954	Al^{+3} intercalated
4955	Acidified ethylene diamine treated
5030	Zironyl ion intercalated

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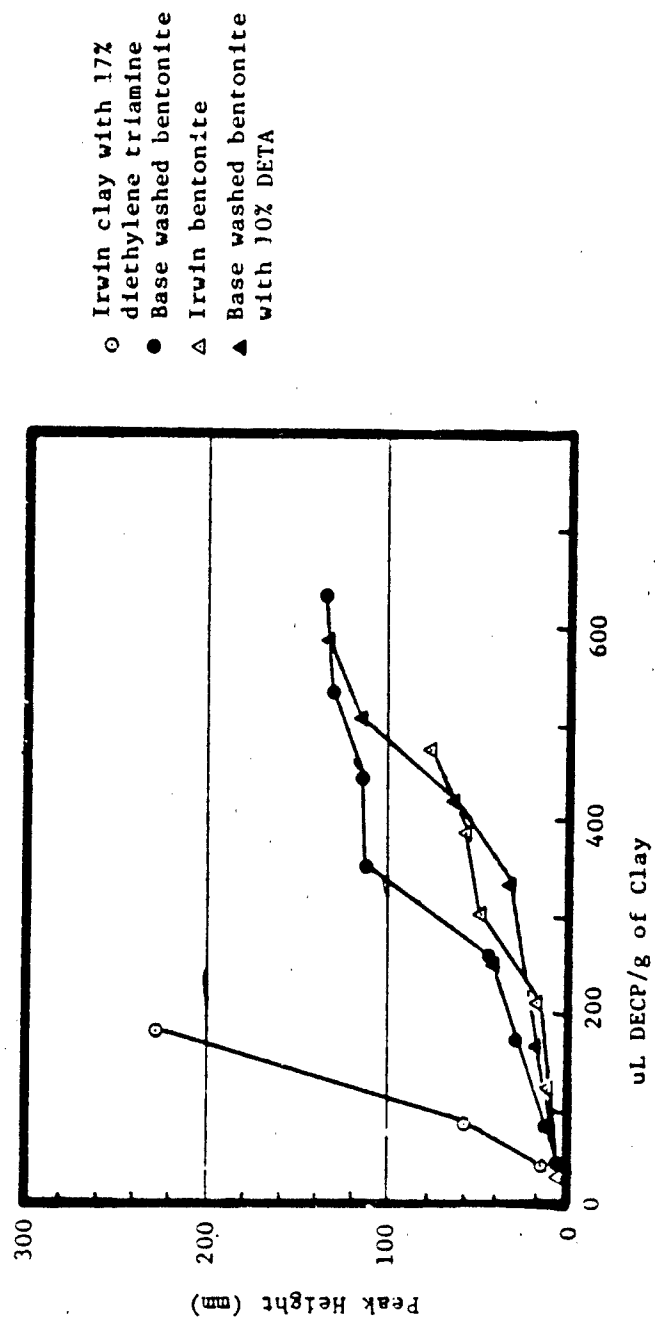
Figure 1. The Evaluation of Irwin Clays in Adsorbing DECP Using the Headspace Method (Section II.A).

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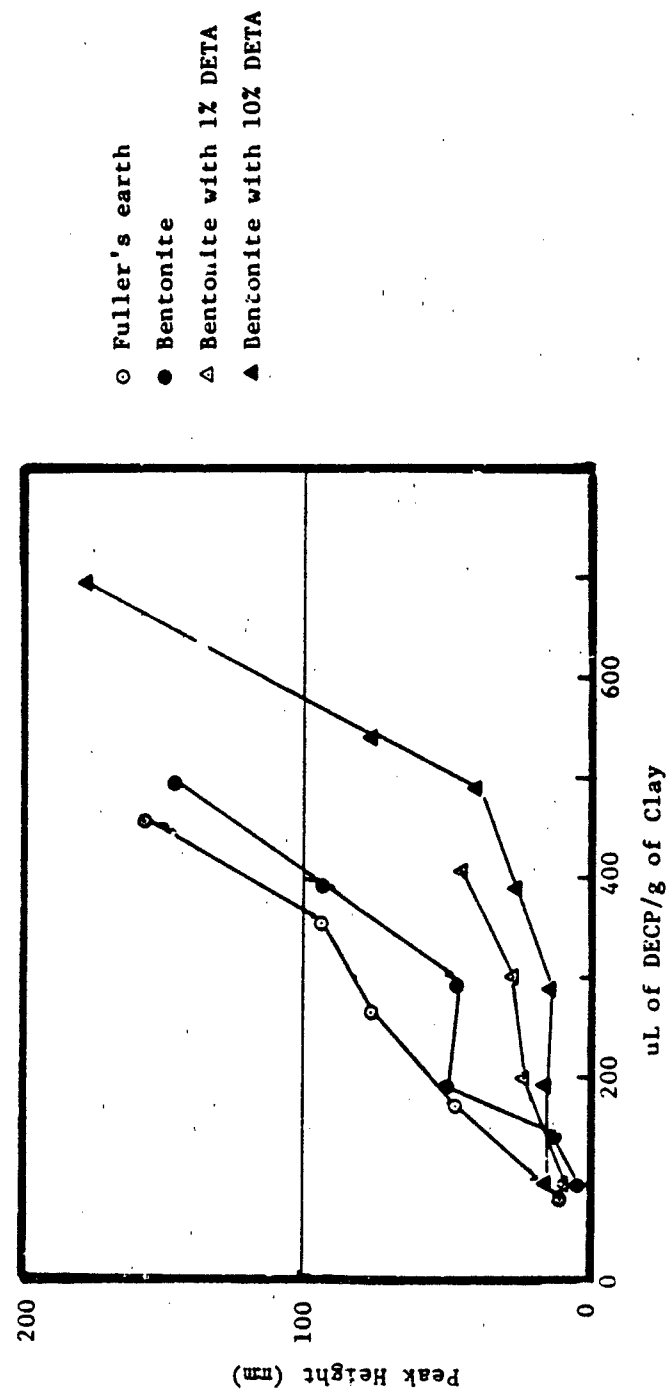
Figure 2. The Evaluation of Bentonite Clays in Adsorbing DECP Using the Headspace Method (Section II.A).

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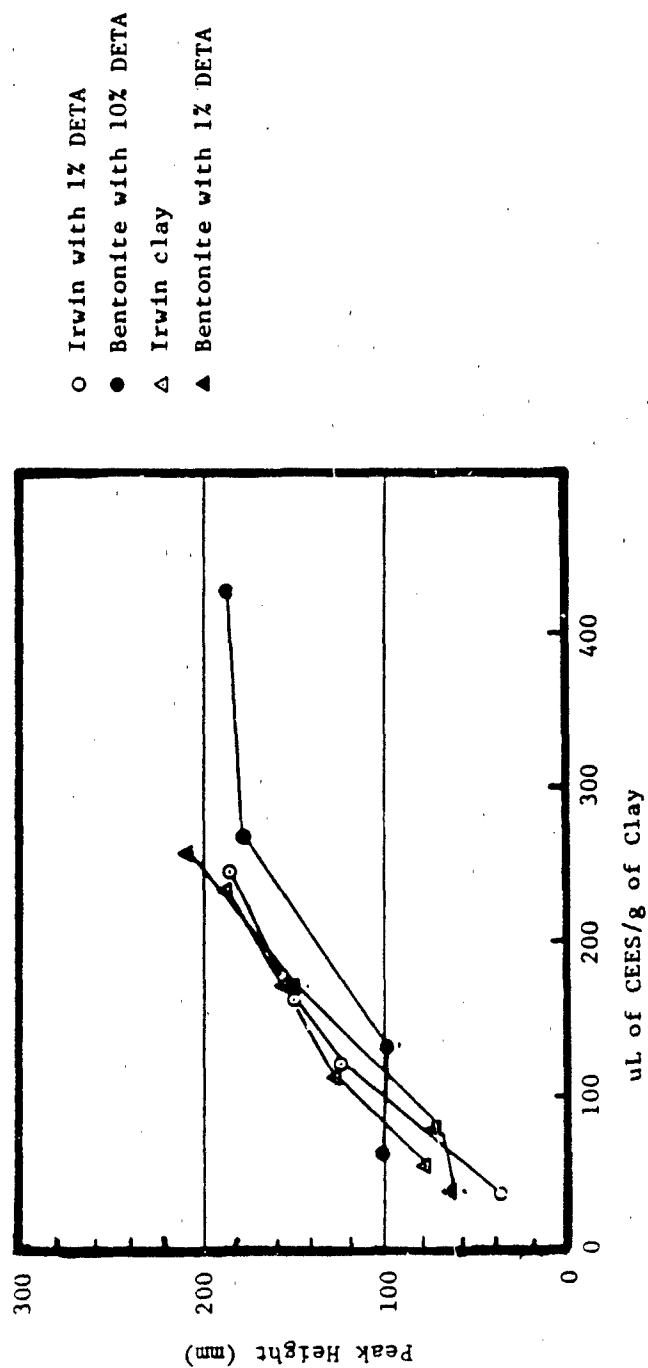
Figure 3. Evaluation of Clays for Adsorption of CEES Using the Headspace Method (Section II.A).
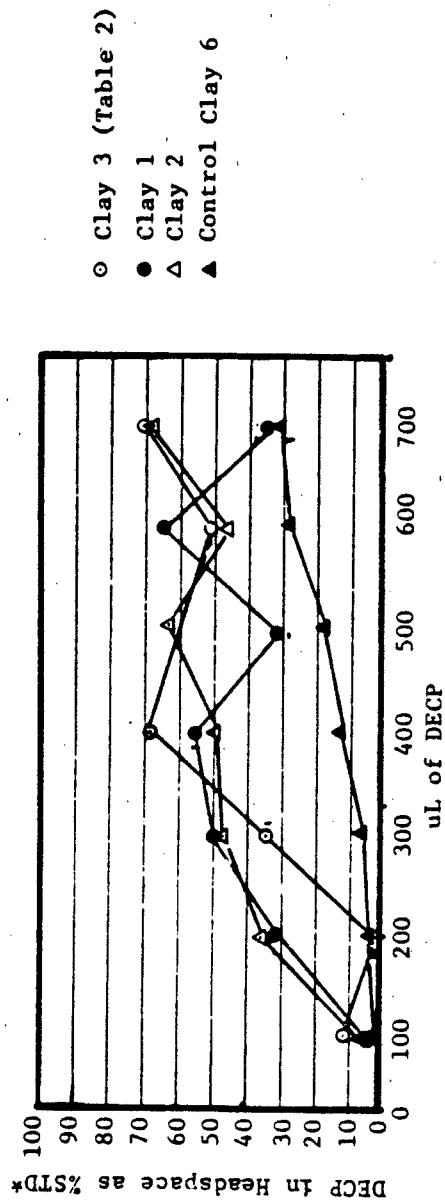
Figure 4. Evaluation of Clays 1, 2 and 3 Against DECP Using the Headspace Analysis Method (Section II.A).
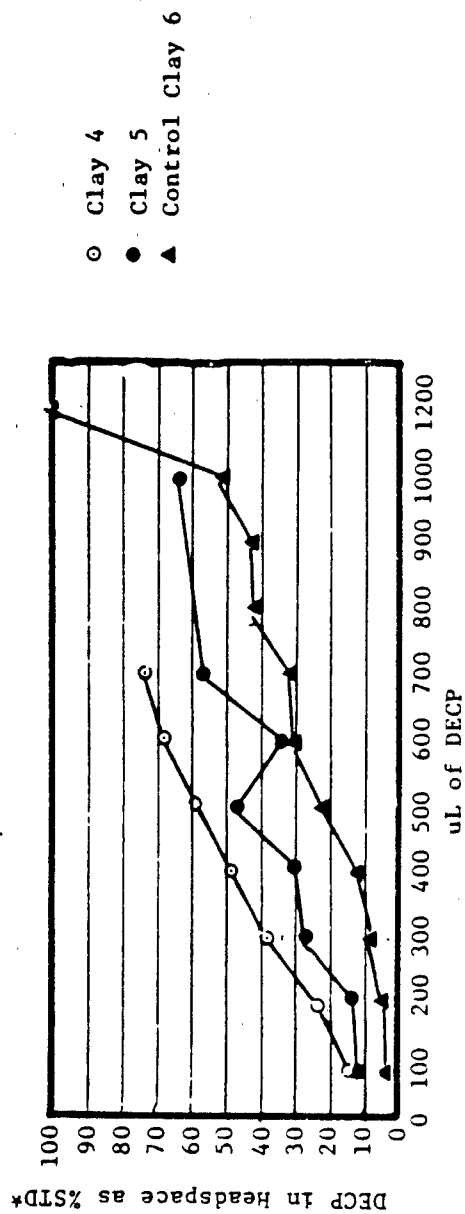
*STD = Neat DECP

Figure 5. Evaluation of Clays 4 and 5 Against DECP Using the Headspace Analysis Method (Section II.A).

*STD = Neat DECP

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Decomposition of DECP by Clays
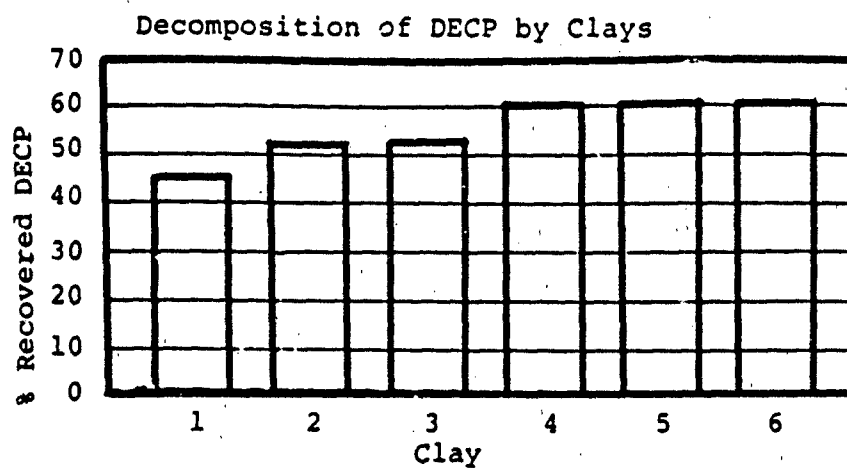
Figure 6.   The Analysis of the Extract from the Clays
Treated with DECP in the 6 Minute Test
(Section II.B)

Decomposition of DECP by Copper Treated Clays
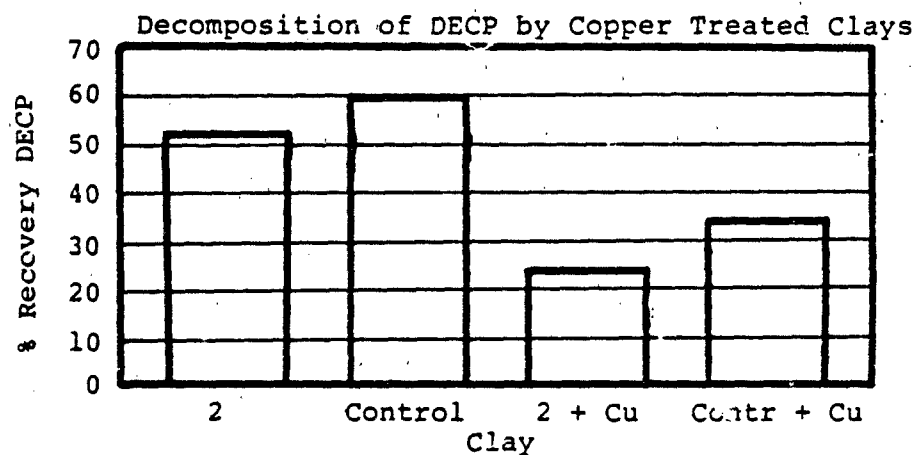
Figure 7.   The Effect of Copper Ion on the Decomposition
of DECP

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3. Kinetic Runs

Several 200 mg samples of clay were weighed into separate vials and spiked with 5 uL of neat CEES. The mixture was treated as in Method 1; the time from CEES addition to addition of 2 mL of ether was measured. A 3 µL sample of the extract was analyzed by GC-AFID. A regression analysis[4] of the natural ln/ln plot was used to obtain the data given in Table III.

The difficulty with Methods 1 and 2 was the possibility that the capacity of the clay had been exceeded. Method 1 resulted in peak heights ranging from 75-93% of those standards, which were prepared by adding the standard amount of CEES to an equal volume of extracting solvent. When the amount of simulant added to the clay was decreased by 50% (i.e., Method 2) and the standing time increased, the resulting peak heights decreased to 30-72% of those of standards. Results of the comparison between methods are presented in Table IV.

D. Procedures for Comparing the Reaction of DECP with Clays

1. Method 1

A sample of 200 mg of clay was weighed into a vial and 40 µL of DECP was added. The mixture was stirred on a vortex mixer and allowed to stand for 5 minutes. The clay was extracted with 2 mL of ether and the extract was diluted 1:100 before analysis by GC-AFID.

2. Method 2

A sample of clay was treated with 2 mL of an ethereal solution of 1 µg/mL DECP. A 3 µL sample of the solution was analyzed at different times to allow measurement of reaction kinetics.

3. Method 3

A sample of clay was treated with 5 µL of DECP as in Method 1, except that the ether extracted was diluted 1:10.

4. Method 4

A sample of clay was treated with 10 µL of DECP as in Method 3.

TABLE III

REGRESSION ANALYSES[4] ON KINETIC RUNS OF CEES

[ln (% simulant remaining vs. ln (time)]

Clay	Y-Intercept	Slope	r^2	t	sy·x	Degrees of Freedom
1	3.90	-1.18	0.97	-11.35	0.24	4
1w/Cu^{2+}	3.80	-0.65	0.90	-6.13	0.25	4
4374T	4.37	-1.03	0.97	-11.30	0.21	4
4374Tw/Cu^{2+}	4.18	-0.73	0.96	-9.43	0.18	4
4375T	4.35	-0.93	0.95	-7.53	0.24	3
4375Tw/Cu^{2+}	4.53	-0.47	0.83	-4.40	0.25	4
3	3.67	-1.06	2.00	-33.50	0.07	4
3w/Cu^{2+}	3.80	-0.55	0.98	-16.04	0.08	4
4	3.58	-0.90	1.00	-36.49	0.06	4
4w/Cu^{2+}	3.82	-0.52	0.99	-21.92	0.06	4
5	3.41	-0.75	0.98	-13.36	0.13	4
5w/Cu^{2+}	3.80	-0.37	0.97	-10.91	0.08	4
6	4.20	-1.25	0.98	-15.34	0.19	4
6w/Cu^{2+}	4.25	-0.82	0.96	-9.22	0.21	4

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TABLE IV

COMPARISON OF METHODS IN SECTION II.C

Method and duration of simulant/clay contact for CEES. Values expressed as % simulant remaining.

Clay	Method 1 (5 min)	Method 2 (15 min)	Kinetic (5 min)
Control	78	30	7
4375	79	44	14
4374Tw/Cu^{2+}	83	48	19

5. Kinetic Runs with DECP

Samples of 200 mg of clay were weighed into separate vials and 5 µL of a 20% solution of DECP in ether was added to each. After 1 minute of mixing using a vortex mixer, the vials were allowed to stand t* minutes and 2 mL of ethyl ether was added. The extract was mixed 30 seconds using the vortex mixer, and the clay allowed to separate. A 3.0 µL portion of the extract was analyzed by GC-AFID. The results are given in Table V.

The difficulty encountered with Method 1 was the possibility of exceeding the capacity of the clay by adding excessive simulant. In this case, differences in reaction rates would not be observable in a suitable time period. Method 2 was abandoned, as we felt the use of a dilute solution did not closely relate to a "real world" situation. The method ultimately chosen required addition of only 5 µL of a 20% ethereal simulant solution to the clay. The clays reacted rapidly with simulant added in this mode. (Example: 41% of standard in 5 minutes for 4375T/Cu^{++}). It was felt that the ether added (4 µL) would not interfere with or affect the reaction but would allow improved precision as compared to a 1 µL volume of neat material.

Another consideration was the physical effect of adding relatively large volumes to the clay samples. With both CEES and DECP, larger spikes (20 and 40 µL) led to clumping of the clay which could not be alleviated by agitation, using the vortex mixer. Clumping could affect precision if it prevented reproducible interaction between simulant and clays.

E. The Washer Test for Evaluation of Reactivity of Treated Clays Using Chemical Agent Detector Paper, VGH ABC-M8

Steel washers having an inside diameter of 10 mm and thickness of 1.5 mm were used for the tests. The experimental procedure is outlined below.

1. Packing of Washers with Treated Clay

a) VGH ABC-M8 paper* was placed on a glass plate which, for easy bottom side viewing, was positioned a few inches above a mirror.

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*The VGH ABC-M8 paper was obtained from the Contract Officer's Technical Representative, Dr. Millard Mershon.

TABLE V

REGRESSION ANALYSES ON KINETIC RUNS OF DECP

[ln (% simulant remaining vs. ln (time)]

Clay	Y-Intercept	Slope	r^2	t	sy.x	Degrees of Freedom
1	4.17	-0.16	0.84	-6.44	0.09	8
4374T	3.96	-0.21	0.93	-10.17	0.08	8
4374Tw/Cu	4.36	-0.31	0.79	-5.41	0.21	8
4375T	4.28	-0.21	0.90	-10.22	0.09	11
4375Tw/Cu	4.80	-0.66	0.93	-7.88	0.25	5
3	4.39	-0.08	0.97	-13.39	0.02	6
4	4.37	-0.17	0.90	-7.56	0.07	6
5	4.41	-0.14	0.91	-7.64	0.06	6
6	4.44	-0.10	0.86	-6.12	0.05	6
6w/Cu	4.51	-0.35	0.92	-5.72	0.18	3

b) Three washers were secured to each piece of paper with glue.

c) Enough finely ground clay was added with a micro-spatula to the center of the washer to overfill it.

d) Pressure was applied to the clay with a microscope slide rotated in the lateral plane, thus packing the clay into a disc. More clay was added to the center of the pellet and compressed with the slide until the central hole was completely packed with clay. This packing method resulted reproducibly in clay loads of about 200 mg, determined by weighing replicate clay samples.

2. Addition of Simulant to Clay Pellet Contained by Washer

a) The disc of clay was spiked with simulant measured using a microliter syringe. The syringe was held vertically with the tip of the needle less than 1 cm from the surface of the clay.

b) A stopwatch was started immediately upon spiking.

c) After 4 minutes, if no sign of simulant was seen on the bottom surface of the clay, a second spike was applied. This process was repeated at 4 minute intervals until interaction of the simulant with the detector paper was observed.

d) The time when the simulant was first detected was recorded.

Tables VI, VII and VIII present the results obtained with the various treated clays. The greater the reported time, the more effective the clay in reacting with or adsorbing the simulant.

F. 4 Minute Kinetic Runs with CEES and DECP

Samples of 200 mg of treated clays were weighed into separate vials and 5-100 µL of neat CEES or DECP was added to each. After 1 minute of mixing using a vortex mixer, the vials were allowed to stand 3 additional minutes; 2 mL of ethyl ether was added and the powder extracted well by vigorous stirring for 30 seconds with the vortex mixer. The clay was allowed to separate and was centrifuged. A 3.0 µL portion of the extract was analyzed by GC-AFID. A solution of known concentration was used as a standard. The results, expressed as a percentage of simulant remaining, are given in Table IX and Figures 8 and 9.

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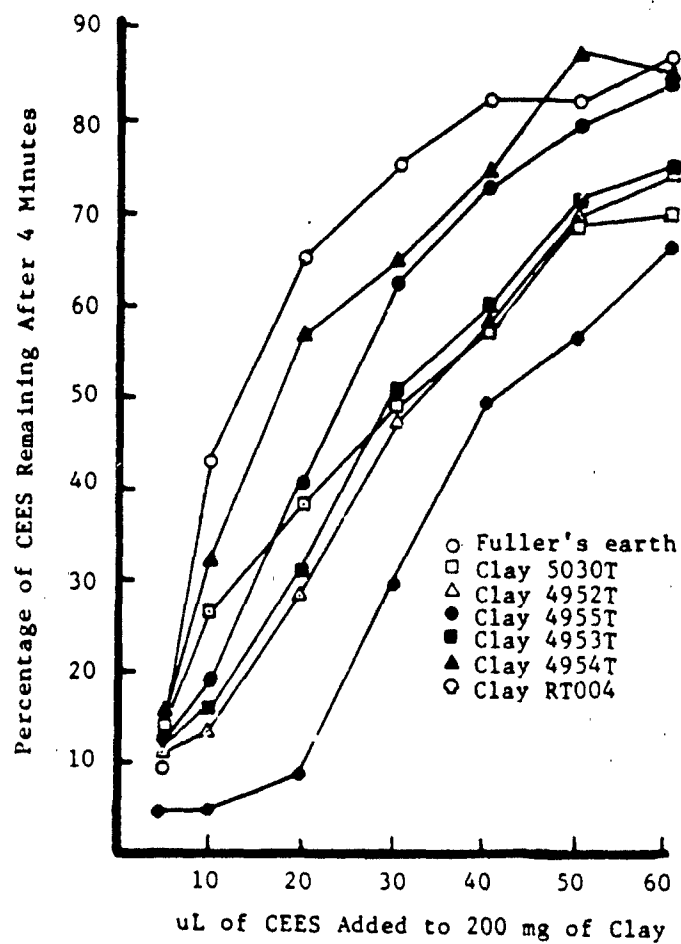
Figure 8.   The Results of the 4 Minute Decomposition Method
with Modified Clays.

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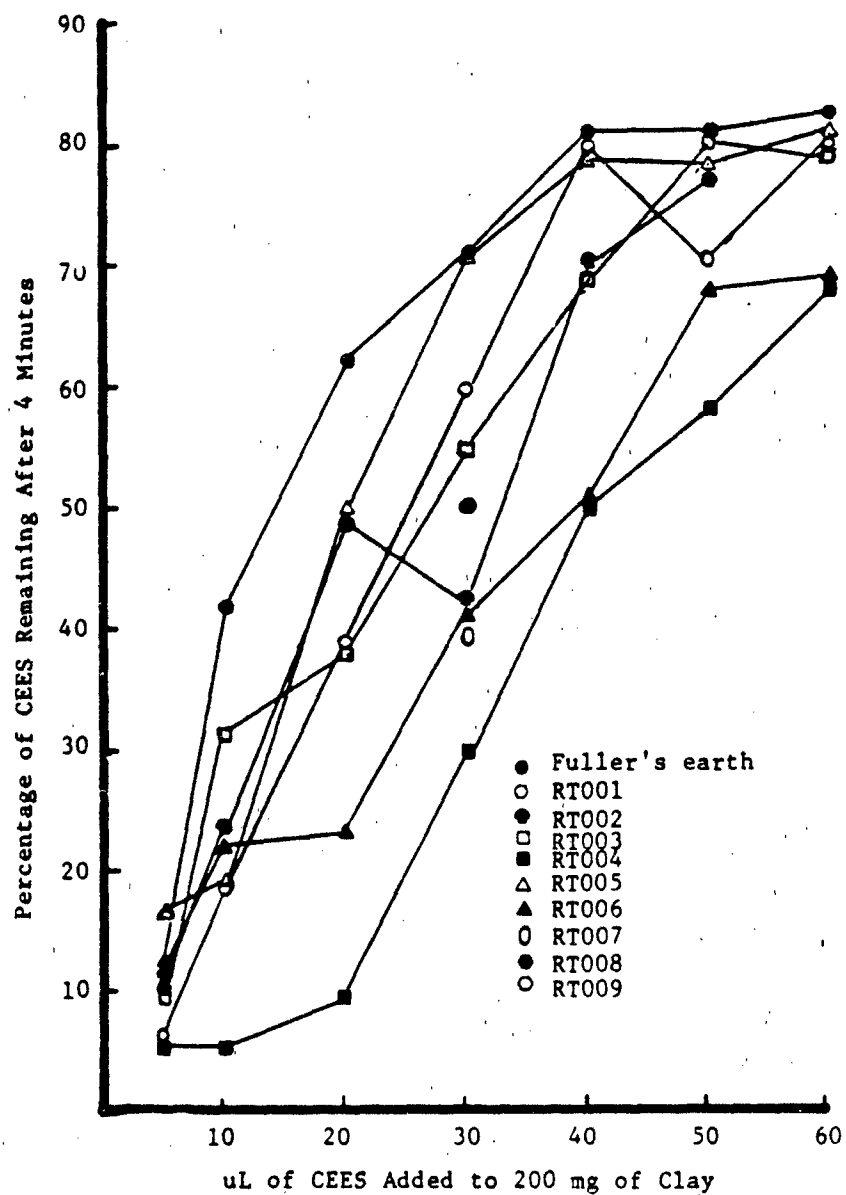
Figure 9. The Results of the 4 Minute Decomposition Method with Modified Clays.

TABLE VI

RESULTS OF SPIKING* CLAY PELLETS
WITH CEES

| Clay | Time at Which Colored Spot First Appeared (min:sec) | | |
	Replicate #1	Replicate #2	Replicate #3
#1	9:50	9:45	
#2	5:15	8:00	
#3	6:40	5:30	
#4	8:40	5:30	
#5	12:30	3:45	12:15
#6	10:45	9:00	
Crude Sodium Bentonite	11:15	4:45	8:30
Sodium Bentonite w/1% Amine	13:20	9:30	
Sodium Bentonite w/10% Amine	3:00	6:45	
Crude Irwin	4:50	5:45	
Irwin w/1% Coupled Amine	7:40	7:00	
Fuller's Earth	8:40	12:30	
4374T	5:30	3:50	
4375T	9:45	6:15	
#6 w/Cu^{2+}	17:30	19:35	
4374Tw/Cu^{2+}	10:15	10:15	
4375Tw/Cu^{2+}	11:30	9:15	

*Clays were spiked with 10 µL of neat simulant at time zero, then repeat spikes were made at 4 minute intervals (i.e., 0, 4, 8, 12....).

TABLE VII

RESULTS OF SPIKING* CLAY PELLETS WITH DBCP

Time at Which Colored Spot First Appeared (min:sec)

Clay	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5
#1	19:20	22:30			
#2	22:45	25:00		34:00	
#3	42:30	27:45	27:00		
#4	21:20	23:15			
#5	32:45	23:45	31:45	21:30	
#6	30:15	35:30	26:45	33:00	
Crude Sodium Bentonite	23:45	21:00			
Sodium Bentonite w/1% Amine	10:00	18:00	29:00	20:20	
Sodium Bentonite w/10% Amine	2:40	7:00	5:00	6:15	
Crude Irwin	22:10	18:00	25:00	19:41	
Irwin w/1% Coupled Amine	15:00	8:30	9:30	9:20	
Fuller's Earth	20:15	25:15	47:30	37:00	25:00
4374T	13:45	11:15			
4375T	22:00	28:30	37:00	38:30	
#6 w/Cu2+	24:30	18:00	13:45	20:30	
4374Tw/Cu2+	6:15	18:45	18:45	13:00	
4375Tw/Cu2+	17:45	13:45			

*Clays were spiked with 50 μL of neat simulant at time zero, then 20 μL thereafter at 4 minute intervals (i.e., 50 μL, t=0, 20 μL, t=4, 9, 12, 16, 20....).

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TABLE VIII

RESULTS OF WASHER TESTS ON CLAYS 4952-4955

Washer

CEES[a]

Clay	Replicate	Interaction Time (min)
4952	1	27.00
	2	32.30
	3	20:15
4953	1	26:00
	2	23:30
	3	31:00
4954	1	9:00
	2	9:30
	3	9:00
4955	1	25:00
	2	25:30
	3	21:00
Fuller's Earth	1	14:00
	2	12:00
4952T	1	34:30
	2	28:00

DECP[b]

4952	1	55:45
	2	48:00
	3	51:00
4953	1	52:00
	2	54:30
	3	42:30

TABLE VIII. (cont.)

Clay	Replicate	Interaction Time (min)
	DECP[b]	
4954	1	17:00[1]
	2	46:00
	3	70:00[2]
4955	1	50:30
	2	36:30
	3	43:45

[1]Appears to have formed a channel down the side of the pellet.

[2]At around 55:00 minutes simulant seemed to build on upper surface and drain off to side.

[a]Fuller's Earth showed interaction at about 12 minutes.

[b]Fuller's Earth showed interaction at about 30 minutes.

TABLE IX

DECOMPOSITION OF CEES BY CLAYS AFTER 4 MINUTES

Percentage of CEES Remaining After 4 Minutes

Clay	5 μL	10 μL	20 μL	30 μL	40 μL	50 μL	60 μL
RT001	7	18	38	60	81	71	81
RT002	13	26	49	73	72	77	82
RT003	8	33	37	55	69	81	80
RT004	5	5	9	30	50	57	67
RT005	16	18	50	73	79	77	83
RT006	13	24	26	42	52	66	69
RT007				40			
RT008				51			
RT009				43			

Determinations with RT004 were repeated at least four times with deviation of less than 10% from the values reported in Figures 8 and 9, so long as the ambient temperature of the determination was reasonably constant. Subsequent to the preparation of the Draft Final Report the ambient temperature was changed and the temperature dependence of this test was dissolved.

G. Modified Washer Test

The washer test described in E was modified by using a 5 mL round-bottom flask to indent the clay plug uniformly. Attempts to develop a uniform pressure to pack the clay plugs had limited success. The final modification was to pack the plugs until excess clay powder poured over the sides of the washer. The flask was used to indent the surface and the weight of clay was recorded. The simulant was then added (10 μL of CEES or 20 μL of DECP) every 4 minutes. The results, expressed as a factor, μL simulant X time mg of powder, are given in Table X.

H. Procedures for Film Preparation

1. Grafting

The films are graft copolymers prepared by the gamma radiation-initiated polymerization of the desired monomer onto low density polyethylene film. The polyethylene (1.0 mil thickness, 14 in x 25 ft) was interleaved with cheesecloth and rolled around a 0.5 inch aluminum rod. The rolled film was placed into a hydrometer jar, which was closed with a rubber stopper containing inlet and outlet tubes. The jar was connected to a manifold and alternately evacuated to 0.5 cm Hg and brought to ambient pressure with N_2 (five cycles) in order to remove oxygen. The jar was evacuated again and the grafting solution (monomer plus solvent) was drawn into the jar to immerse the film roll. The filled jar was placed in the irradiation cell and exposed to cobalt-60 gamma radiation at 12,000 rads/hour for 68 hours. Total applied radiation dose was 0.811 Mrad.

After standing overnight, the jar was opened and the grafted film was separated from the cheesecloth backing, washed three times with a suitable solvent to remove any homopolymer, and air-dried.

Grafting solution compositions for the films reported in this period are:

BD-1	20 wt %	2-vinylpyridine
	80 wt %	methanol
BD-2	25 wt %	4-vinylpyridine
	75 wt %	methanol

TABLE X

TIGHTLY PACKED WASHER TEST WITH CEES

Material	Wt	Breakthrough Time min:sec	Total Simulant μL	Simulant μL X sec/mg
Fuller's Earth	190	4:30	20	28
	186	4:27	20	28
RT004	175	9:00	30	93
	159	9:35	30	108
RT006	84	5:00	20	72
	81	1:35	10	12
	94	1:47	10	11
RT007	95	0:13	10	1
	108	1:30	10	8
RT008	104	15:10	40	352
	96	10:30	30	198
RT009	82	6:05	20	90
	88	5:35	20	76

BD-3	25 wt %	4-vinylpyridine
	1 wt %	divinylbenzene
	74 wr %	methanol
BD-4	25 wt %	vinylbenzylchloride
	75 wt %	methanol
BD-5	25 wt %	vinylbenzylchloride
	75 wt %	benzene

2.   Preparation of Periodide Films

Samples of the three quaternized films (3 ft'', ca.
12 g) were placed in separate 1L wide-mouth jars. To each was
added 330 mL of KI-I_2 solution (0.2 N in KI_3) along with suffic-
ient deionized water to fill the jars to within 1 inch of the
top. The capped jars were agitated on a reciprocating platform
shaker for 48 hours. The films were transferred to 3L stainless
steel beakers and washed five times with 2L portions of deionized
water and dried overnight between absorbent paper toweling.
Film BD-3-Q-I_3 disintegrated upon washing and was discarded.
The remaining two lustrous, red-black films were stored in amber
bottles.

Film designations: BD-1-Q-I_3
                      BD-2-Q-I_3

3.   Alternative Preparation of Periodide Films

Samples (6 in x 6 in) of each of the three films BD-1-Q,
BD-2-Q and BD-3-Q were placed in separate 50 mL Erlenmeyer flasks.
To each flask was added 350 mL of chloroform containing 3 g
of I_2. The stoppered flasks were shaken overnight. Each film
was washed four times with 300 mL portions of chloroform. The
cross-linked film (BD-3-Q) disintegrated upon washing. The
two remaining films were dried between absorbent paper toweling.
The two remaining films (lustrous, red-black, flexible) were
stored in amber bottles.

Film designations: BD-1-Q-I_3 ($CHCl_3$/I_2)
                     BD-2-Q-I_3 ($CHCl_3$/I_2)

4.   Preparation of Azide Films

Samples of films BD-1-Q, BD-2-Q and BD-5-Q (1 ft')
were placed in separate 1L jars. To each jar was added 200
mL of 0.2 M sodium azide and 500 mL of deionized water. After
shaking for 2 days on a reciprocating platform shaker, the films
were removed from the jars, washed four times with 2L portions

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of deionized water, and dried overnight between layers of absorbent toweling. Film BD-1-Q (colorless, transparent), Film BD-2-Q (pale blue, translucent), and Film BD-5-Q were stored in amber bottles.

Film designations: BD-1-Q-N$_3$
BD-2-Q-N$_3$
BD-5-Q-N$_3$

5. Preparation of Hydroxide Films

Samples of BD-1-Q (0.6 ft'), BD-3-Q, and BD-5-Q (1.0 ft') were placed in separate 1L wide-mouth jars. To each jar was added 500 mL of deionized water containing 20 g of potassium hydroxide. The capped jars were agitated overnight (ca. 18 hours) on a reciprocating platform shaker. The films were removed from the jars and washed with six 2L portions of deionized water until the washings were neutral to pH paper. The colored films (BD-1-Q amber; BD-3-Q blue-green) were air-dried between layers of absorbent paper and stored in amber bottles. BD-5-Q-OH was colorless.

Film designations: BD-1-Q-OH
BD-3-Q-OH
BD-5-Q-OH

6. Preparation of Thiosulfate Film

Approximately 2 ft' (ca. 8 g) of quaternized BD-2 films (BD-2-Q and BD-5-Q) were placed in a 1L wide-mouth jar along with 800 mL of deionized water containing 40 g of sodium thiosulfate. The capped jar was agitated for 24 hours on a reciprocating platform shaker. The film was removed, washed five times with 2L portions of deionized water, and air-dried between layers of absorbent paper. The faint yellow film was stored in an amber bottle.

Film designation: BD-2-Q-S$_2$O$_3$
BD-5-Q-S$_2$O$_3$

The procedures in the preceding paragraph were repeated to yield the chlorate, perchlorate, permanganate, dichromate, hypochlorite, m-chloroperbenzoate and related polymers of BD-5-Q film.

7. Preparation of Chlorochromate Films

Chromium trioxide (CrO$_3$, 9.8 g) was added with stirring to hydrochloric acid (1.65 M, 60 mL). The resulting clear orange solution was divided into two 30 mL portions and each portion

wa. added to a 1L wide-mouth jar containing 1 ft^4 (ca. 4 g) of either BD-1 or BD-2 film in 450 mL of cold (0-5°C) deionized water. After standing in an ice bath for 30 minutes, the capped jars were agitated on a reciprocating platform shaker for 48 hours. The films were removed from the jars, washed five times (2L/wash) with deionized water, air-dried between layers of absorbent paper, and stored in amber bottles.

Film designations: BD-1-HCrO$_3$Cl
                     BD-2-HCrO$_3$Cl

    8.   Preparation of Perbromide Film

        Samples of the films BD-1, BD-2, and BD-3 (3 ft^4 each, ca. 12 g) were placed in separate 1L wide-mouth jars. To each jar was added 250 mL of the reagent (120 mL of conc. HBr + 40 mL of Br$_2$/L and 500 mL deionized water). The capped jars were placed on a reciprocating platform shaker and agitated overnight. The excess reagent was decanted and the films were transferred to 3L stainless steel beakers and washed five times with 2L portions of deionized water. The washed films were placed between layers of absorbent paper toweling and air-dried overnight. After drying, the cross-linked film prepared from BD-3 was extremely brittle and disintegrated upon handling. The other two films (reddish-brown) were stored in amber bottles.

Film designations: BD-1-HBr$_3$
                     BD-2-HBr$_3$

    9.   Quaternization of Grafted Films

        Approximately 3 ft^4 of each film (ca. 12 g) were placed in 1L Erlenmeyer flasks. To each flask was added 750 mL of reagent grade methanol containing 30 mL of methyl iodide. The stoppered flasks were agitated for 3 days on a reciprocating platform shaker. The films were removed, washed twice with methanol, and air-dried.

Film designations: BD-1-Q
                     BD-2-Q
                     BD-3-Q

        Approximately 3 ft^4 of film grafted with 4-chloromethyl-styrene was treated with trimethylamine in methanol. The mixture was agitated for 3 days and the film washed with water and air-dried.

    Film designation: BD-5-Q

    The films prepared and tested are given in Table XI.

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TABLE XI

SIMULANTS TESTED

Film Designation	HD Simulant CEES	GB Simulant DECP	VX Simulant EEMPT	GR Simulant DNPP
BD-1-HBr$_3$	+			
BD-1-HCrO$_3$Cl	−		−	
BD-1-Q-I$_3$	−			
BD-1-Q-OH	−			+
BD-1-Q-S$_2$O$_3$				
BD-1-Q-N$_3$	−			
BD-2-HBr$_3$	+		−	
BD-2-HCrO$_3$Cl	−			
BD-2-Q-I$_3$	−			
BD-2-Q-S$_2$O$_3$	+	+	−	+
BD-2-Q-N$_3$	−			
BD-3-Q-OH				
BD-5-Q-OH	+	+	+	+
BD-5-Q-N$_3$	+	+		++
BD-5-Q-ClO$_3$	−	−		
BD-5-Q-ClO$_4$	−	−		
BD-5-Q-MnO$_4$	−	−dry; ++wet	−dry; −wet	
BD-5-Q-Cr$_2$O$_7$	−	−dry; +wet	−	
BD-5-Q-mClμCO$_3$$^-$	−	++	+/−	
BD-5-Q-BO$_3$	−	+++	+/−	
BD-5-Q-S$_2$O$_8$	+/−	+/−		
BD-5-Q-S$_2$O$_3$	+/−			

TABLE XI. (cont.)

Film Designation	HD Simulant CEES	GB Simulant DECP	VX Simulant EEMPT	GB Simulant DNPP
S-83 ACRYLATE + Cu^{++}(NH$_3$)$_2$	-	-	-	
S-83 ACRYLATE + CuSO$_4$)	+	+		

CEES - Chloroethyl ethyl sulfide "Mustard"
DECP - Diethyl chloro phosphate
EEMPT - O-Ethyl-S-Ethylmethylphosphonothionate
DNPP - Deithyl-p-nitrophenylphosphate

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10. Ion Exchange Capacity

Portions of each air-dried film were weighed (BD-5-Q-OH, 1.414 g, and BD-5-Q-Cl, 1.2971 g) and placed in separate clean 250 mL Erlenmeyer flasks. To BD-5-Q-OH was added 100.0 mL of 0.10 N HCl and to BD-5-Q-Cl was added 10.0 mL of 40% neutral $NaNO_3$. The stoppered flasks were shaken overnight and the chloride content of the aqueous solutions was determined by ion chromatography.

A sample of 1.4144 g of BD-5-Q-NMe$_3$OH, containing 9.10% moisture* consumed 78 of the 219 chloride "units" in 100 mL of 0.1 N HCl. This equates to an ion-exchange capacity of 2.77 mEq/g (dry wt).

A sample of 1.2971 g of BD-5-Q-Me$_3$Cl, containing 7.46% moisture,* released 71.5 chloride units when treated with sodium nitrate. The standard of 3.56 μg/mL gave 219 chloride units. The ion-exchange capacity of the sample chloride was calculated from these data as 2.71 mEq/g (dry wt).

I. Nerve Agent Simulant Diethyl p-Nitrophenylphosphate

1. Preparation of Standards

Aqueous solutions of 4-nitrophenol (Aldrich 13,023-0) and diethyl-p-nitrophenylphosphate (DNPP) (Aldrich 85,579-0) were prepared gravimetrically to yield stock solutions of 1.02 x 10^{-2} M and 9.01 x 10^{-3} M, respectively. Working solutions were prepared by 1:100 dilution of the stock with deionized (milli-Q) water. All solutions were stored at 40°C in the dark.

2. Visible and Ultraviolet Absorption Spectra

Absorption spectra were determined using a Varian-Cary Model 219 UV/VISIBLE recording spectrophotometer. All measurements were made using fused silica cells having a nominal path length of 1 cm.

Grafted derivatized films were cut into 13 x 50 mm strips. These strips were inserted diagonally into the spectrophotometer cuvet, reagent solution was added, and after the desired time interval the strip was withdrawn and either the entire spectrum scanned or the absorbance at a specific wavelength measured.

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*Moisture based on weight loss of film on heating under reduced pressure.

The films were treated with DNPP in aqueous solution. The absorbance at 273 nm, the most prominent maximum exhibited by DNPP, was followed over time. These experimental results are presented in Table XII.

J.   Preparation of Indicator-Treated Film BD-5-Q-NMe$_3$$^+OH^-$

A 10 cm x 20 cm piece of BD-5-Q-N-Me$_3$$^+OH^-$ was swirled for 60 seconds with 100 mL of 100 µg/mL methanolic phenolphthalein solution. The film rapidly became pink. The pink film was washed twice for 2 minutes with 100 mL portions of fresh methanol and air-dried. Other indicator solutions were used to prepare a variety of dyed films. These are listed in Table XIII.

K.   Reactions of Simulants with Grafted Films

1.   Diethyl Chlorophosphate

A 3 cm x 3 cm piece of grafted film was placed into a septum-sealed 4 mL vial. One or 2 mL of an ethereal solution of DECP (41.9 µg/mL) was placed in the vial, which was placed on a reciprocating shaker. The concentration of DECP was followed over time by analysis of the ethereal solution using GC. The initial rate of the film/simulant reaction was calculated as the initial slope of the simulant concentration vs. time curve.

The GC analytical conditions for DECP from clay head-space or solutions, used for the evaluation of reactive films, are given below:

Column: 8 ft x 2 mm-I.D. 3% OV-1 on Supelcoport (100/120 mesh)

Oven Temperature: 125 isothermal

Detector Temperature: 250°C

Injector Temperature: 150°C

Carrier/Flow Rate: He/40 mL/min

Detector: Alkali bead, flame ionization

2.   Mustard Simulant-Chloroethyl Ethyl Sulfide

a)   A 3 cm x 3 cm piece of grafted film was placed in a septum-sealed vial, 1.0 mL of a 100 µg/mL hexane solution of CEES was added to the vial and the concentration of CEES was monitored over time by GC.

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TABLE XII

ABSORBANCE AT 273 NM OF 9.01 X 10^{-5} M
DNPP AFTER INCUBATION WITH
GRAFTED DERIVATIZED FILMS

Film Designation	Time After Placement of Film in Solution (minutes)	Absorbance at 273 nm
BD-1-Q-OH	0	0.79
	9	0.78
	45	0.77
	133	0.76
	1121	0.68
BD-3-Q-OH	0	0.80
	64	0.57
	232	0.49
	342	0.26
BD-2-Q-S_2O_3	0	0.80
	238	0.36
	347	0.14
Control, DNPP + OH$^-$	0	0.77
	18	0.72
	28	0.65
	64	0.52
	226	0.24
	1440	0.15
Control, DNPP Acidified c HCl ($_{max}$ 316)	1440	0.80

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TABLE XIII

COLOR REACTIONS OF INDICATOR FILMS WITH SIMULANTS

Indicator	BD-5-QNMe$_3$OH Film	DECP	CEES
a) Bromothymol blue	Dark Blue	Green-Yellow	Dark Blue
b) Cresol Red	Dark Red	Lightened Orange	Red
c) Bromocresol green-Methyl red	Dark Green	Yellow	Dark Green
d) Dibromo-o-cresol sulfonaphthalein	Dark Purple	Yellow	Dark Purple
e) 4,5-Dihydroxy-3(p-sulfophenyl azo-2,7-naphthalene disulfonic acid trisodium salt	Dark Red	Red	Dark Red
f) Janus green B	Colorless		
g) Potamine fast green GL	Green	Green	Green
h) Potamine green 26B	Dark Green	Dark Green	Dark Green
i) HACH wide range H indicator	Green	Orange	Green
j) Phenolphthalein	Pink	Colorless	Green

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TABLE XIII. (cont.)

Indicator	BD-5-QNMe₃N₃ Film	DECP	CEES
a)	Blue	Green Yellow	Blue
b)	Dark Red	Yellow	Red
c)	Blue	Green	Blue
d)	Blue	Green	Blue
e)	Dark Red	Red	Dark Red
f)	Colorless		
g)	Green	Green	Green
h)	Dark Green	Dark Green	Dark Green
i)	Blue Green	Orange	Blue

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TABLE XIII. (cont.)

Indicator	BD-5-QNMe$_3$S$_2$O$_3$ Film	DECP	CEES
a)	Green	Yellow	Green
b)	Yellow	Orange	Yellow
c)	Light Blue	Colorless	Light Blue
d)	Dark Blue	Green-Yellow	Dark Blue
e)	Violet	Violet	Violet
f)	Colorless		
g)	Colorless		
h)	Light Green	Light Green	Light Green
i)	Blue	Lightened Yellow	Blue

b) A 3 cm x 3 cm piece of grafted film was placed in a septum-sealed vial; 1.0 µL of CEES was applied to the film surface using a Hamilton syringe. The reaction was quenched by addition of 1.0 mL of diethyl ether to the vial and analysis of the solution by GC as above. Multiple samples were used to observe the effect of time.

The GC analytical conditions for CEES from clays and films are given below:

Column: 6 ft x 4 mm I.D. 5% OV-1 on Chromosorb W

Oven Temperature: 70°C isothermal

Detector Temperature: 250°C

Injector Temperature: 250°C

Carrier/Flow Rate: He/40 mL/min

Detector: Flame Ionization

L. VX Simulant O-Ethyl-S-ethylmethylphosphonothioate

A 9 cm² sample of film was wetted with 1 mL of a solution of EEMPT in ether (2.43×10^{-3} M). EEMPT in the film was analyzed by GC over 3 hours. No loss of simulant was observed. The evaluation was repeated with a 1:10 dilution of the solution; however, again no loss of EEMPT could be observed.

Samples of 9 cm² of the phenolphthalein-treated BD-5-Q-NMe$_3^+$OH$^-$ were treated with 1 µL samples of EEMPT. The color of the film was lost at the contact points. The film was folded to increase the contact surface with the EEMPT. At specific times the reaction was quenched by adding 4 mL of ether. After thorough extraction of the film, the solution was analyzed by GC. The results showed 40% removed at 1.5 hours; 52% removed at 2.5 hours; and 61% removed at 3.5 hours.

The results of the films are summarized in Table XI.

III. RESULTS AND DISCUSSION

A. Introduction

The detoxification of chemical and biological agents can occur by a number of mechanisms, by adsorption or by nucleophilic or oxidative reactions. This project was designed to test the possibility of developing reactive films and powders with adsorptive or nucleophilic and/or oxidative activity by grafting reactive groups onto polyethylene films and then forming quaternary salts from these functions. Nucleophilic and oxidative anions were then added as counterions of the quaternary ammonium ion. Indicator dyes were added to some of these films to evaluate them as detectors for chemical agents.

Native Irwin or bentonite clays were processed by Anglo-American Clays Corporation by proprietary processes to beneficiate the clays or to introduce reactive amines, large surface areas, or metal ions intercalated between the layers. These activated clays had the potential for providing nucleophilic or oxidative reactivity by catalytic processes. The processing also increased the adsorptive capability of the clays. The properties of these clays which are available to SwRI are given in Table II.

The effectiveness of these decontaminating agents was evaluated by use of simulants with reactivities similar to those of the common chemical agents. The experimental methods for determining the effectiveness of the films and clays in decomposing the simulants proved to be difficult to develop; however, satisfactory methods were found. The simulants are given in Table I.

B. Choice of Simulants

Chloroethyl ethyl sulfide (CEES), the simulant for the blister agent mustard (HD), was selected for its similarity in reactivity to HD. CEES was obtained from Aldrich Chemical Company and used without any further purification. The β-chloroethyl group is subject to nucleophilic displacement and the sulfide group will undergo oxidation to the sulfoxide. In evaluation of the reactive films, diethylsulfide (DES) was used to evaluate the oxidizing power of the film to form diethyl sulfoxide.

The simulants for the G-type nerve agents were also chosen for their similarity in reactivity with the fluoromethylphosphonates. Diethyl chlorophosphate (DECP) and diethyl-p-nitrophenyl-phosphate (DNPP) were obtained from Aldrich Chemical Company and were used without any further purification. They both are highly reactive with nucleophiles.

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The simulant for VX nerve agent was O-ethyl-S-ethyl-5-methyl-phosphorothioate (EEMPT), which was expected to be less reactive to hydrolysis or oxidation than the chemical agent. Thus the successful reaction of EEMPT with a decontamination system would be a strong indication that VX would be detoxified. The EEMPT was obtained from the Contracting Officer's Technical Representative. The properties of these simulants are given in Table I.

C. Clays

    1. Analytical Methods

        The analytical procedures for evaluating the modified clays listed in Table II evolved during the contract period, so no single test procedure was used for all these samples. The effectiveness of the powders could depend on the properties of the powder to undergo reaction with the simulant to produce nontoxic products. Alternatively, the powder could adsorb the simulant so tightly as to reduce the vapor pressure of the simulant, and thus render it nontoxic. The initial test procedures were designed to evaluate the combination of these two effects. This method was the Headspace analysis (Section II.A), which measures the concentration of the simulant in the vapor state above the clay which had been treated with simulant. The results of this test were erratic and did not distinguish between reaction and adsorption. We felt that reaction or irreversible adsorption was more important to measure, since weak adsorption could lead to toxic effects by slow desorption of agent. Thus we evaluated a reactive analytical method called the kinetic analysis. This procedure measured the disappearance of simulant on treatment with the powder and thus measured the reactivity of the powder with simulant.

        a) Headspace analysis

            The first procedure was to inject a known volume of the simulant into a weighed amount of clay and then measure the amount of simulant in the gaseous state in the headspace. Additional simulant was added until the amount of simulant in the headspace approached that found above liquid simulant with no clay added. This method was used to evaluate the samples A'-E'. This procedure should indicate a combined effect of adsorption and chemical reactivity for decontamination and the results are shown in Figures 1 through 5.

            Samples of Irwin (A') and sodium bentonite (B') control clays, these clays grafted with 1% DETA (C' and D'), and sodium bentonite grafted to 10. DETA (E') were received

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from Anglo-American Clays. Clays B' and E' were treated with methanolic sodium hydroxide in an attempt to increase the nucleophilicity of the clay. The infrared spectrum of E', the grafted clay, after base treatment showed that the amine had been removed by the treatment.

All of the clays except E' showed a slow increase in DECP in the headspace as additional simulant was added (Figures 1 and 2), suggesting that the simulant was not reacting with the clay but being adsorbed onto it. However, E' required 500 μL of DECP/g of clay to give a gas chromatography (GC) peak height approaching that observed with neat simulant. This performance was clearly superior to that of clays A'-D'. Also, this clay after treatment with hydroxide was still more effective than the untreated sodium bentonite.

The Surrey Finest Fuller's Earth performed similarly on treatment with DECP, but it was not as effective as clays A'-E'. This was in agreement with the results presented in the Battelle report[1] which showed that clays from the United States were as effective as the Fuller's Earth from Britain in detoxification of chemical agents.

The evaluation with the blister agent simulant CEES showed that clays A'-E' has about the same effectiveness, with E' requiring slightly more simulant to give the GC signal comparable to that of neat simulant. None of the clays were as effective in adsorbing CEES as they were with DECP (Figure 3).

This headspace analytical procedure was used to evaluate the next series of clays, which also had had amine or other nucleophilic moieties added to the structure. The results of the tests are given in Figures 4 and 5. These data suggest that the modified clays were no better than, and perhaps inferior to, the control clay in decreasing the vapor pressure of the simulant DECP. The analytical results, however, showed considerable scatter and did not allow distinction between adsorption and reaction with the simulants.

b)   Kinetic analysis - 6 minute test (see Section II.B and C)

A second procedure was developed for clays 1-6 to detect reaction with simulant. A 200 mg sample of modified clay was treated with 40 μL of DECP and the mixture stirred for 1 minute. After 5 minutes 2 mL of ether was added to the sample. A 1:100 dilution of the ether solution was analyzed by GC using an alkali flame ionization detector (AFID). This method showed that the modified clays 1, 2 and 3 were causing

greater decomposition of the DECP than was the control clay (see Figure 6).

The clays had been shown by Anglo-American Clays to complex with metal ions such as copper. Accordingly the better clay, 2, was treated with copper ion as a 1% solution in ammonia (5 g of clay with 50 mL of solution). The mixture was stirred for 5 minutes, filtered and washed with water and methanol. After drying in an oven at 60°C, the clay was evaluated as before. The results (Figure 7) showed that the copper treatment increased the decomposition of DECP by 100%.

Several experimental approaches were attempted to determine a standard procedure for comparing the adsorption and/or reactivity of these clays. A ratio of 40 μL of simulant such as DECP to 200 mg of clay resulted in the loss of about 30% of the simulant after 5 minutes, regardless of which clay was used. The clay 4375Tw/Cu^{2+} was extracted with ether and the ethereal solution analyzed by GC. Using 1 μL of DECP gave 41% recovery while 10 μL gave 61% recovery and 40 μL gave 66% recovered DECP. This suggests that 40 μL saturated the 200 mg of clay.

c)   Kinetic runs - Variable time (see Section II.D)

For comparative purposes a standard procedure was chosen to provide a crude kinetic measure of the effectiveness of clays 1-6, 4374, and 4375. Several 200 mg samples of the different clays were treated with 5 μL of a 20% solution of DECP in ether. After careful mixing, the samples were allowed to stand for a measured length of time, after which each sample was extracted by addition of 2 mL of ethyl ether with stirring by a vortex mixer. After separation of the clay a 3 μL sample was analyzed by GC using an AFID. The percentage loss of simulant was determined at intervals during the kinetic run.

The results of these kinetic runs were expressed as plots of percent simulant remaining vs. time, which could be expressed linearly, in natural ln/ln plots. In this form the y-intercept indicates the amount of simulant destroyed 1 minute after mixing; the smaller the intercept, the greater the decomposition of simulant. The slope of the curve indicates the rate of further decomposition of the simulant; the more negative the slope, the faster the rate of decomposition. These data are summarized in Tables IV and V.

These data indicate that chemical modification of the clays decreases their effectivneess in adsorbing/reacting with the simulant CEES, as the unmodified control clay (Number 6) produced the greatest disappearance of the simulant. Also,

copper treatment of the clays decreased their effectiveness in destroying CEES. Thus the most effective clay with CEES was the untreated control clay, 6.

With the nerve agent simulant DECP, the situation was different. The untreated control clay was effective in destroying the simulant; however, the clays having ethylene diamine side chains were more effective. Treating the clays with copper increased their effectiveness in each case. The most dramatic effect was exhibited with clay 4375T, which has the ethylene diamine chains only on the surface.

d) "Washer test" - Estimation of adsorption and decomposition

The evaluation using the kinetic analysis (Section II.F) measured the deactivation of simulants by the treated clays based on the amount of unchanged simulant that could be extracted from the clay sample after a given reaction time. This method of analysis measures the amount of simulant which underwent reaction with the clay sample. Any simulant that was ineffectual because of adsorption by the clay would be extracted. Thus the analytical method was not really the best method for estimating the total decontamination potential of the clay by both adsorption and reaction. The analytical method based on evaluation of the simulant vapor in the headspace above the clay samples (Section II.A) did consider the amount of adsorbed simulant; however, this method was difficult to reproduce and required a volatile simulant.

The Contract Officer's Technical Representative, Dr. Millard Mershon, suggested a method for evaluating the combined adsorption and decomposition by measuring the breakthrough time of a plug of clay held in a washer using M8 paper as the detector. This method involved packing the powder or clay in a washer affixed to a sheet of M8 paper. Simulant was added and the time to a color change in the M8 paper was recorded. The details of this procedure are described in Experimental Methods (Section II.E) and the results are summarized in Tables VI and VII. Clay 6 treated with copper sulfate was effective against the HD simulant.

The nerve agent simulant DECP was effectively blocked by clay 4375T, a sodium bentonite clay in which ethylene diamine was attached only to the surface.

These two treated clays were not the best of the series in the extraction test. As might be expected, the adsorptive power of the clay was not directly related to the reactivity of the clay with the simulant.

The reactivity of clays 4952-4955 and 5030 was estimated by the kinetic experiments and the "washer test" (Table VIII). The results in the kinetic test showed that CEES was rapidly destroyed by all of these clays. Only 28-45% of the agent remained after 1 minute and less than 20% at 4 minutes. The decomposition of CEES was probably catalytic with 4952, since doubling the amount of simulant to 10 μL/200 mg did not greatly change the rate of disappearance of CEES: 42% of CEES remained after 1 minute and 18% at 4 minutes.

In another series of tests, 5030T was compared with Fuller's Earth and found to be only slightly more effective. These results also showed the Fuller's Earth to be approximately as effective as the treated clays in this kinetic test.

As was evident from the "washer test," the treated clays had a greater decontamination potential than Fuller's Earth. Probably the kinetic experiments were run with too high a ratio of clay to simulant. Using a larger amount of simulant demonstrated the superiority of the treated clays over Fuller's Earth.

e)   Kinetic test - 4 minute test

The previous methods using 5 or 10 μL of simulant and measuring the simulant remaining at 4 minutes and longer times did not show much difference among the samples of treated clays and Fuller's Earth. Most of these clays gave about 80% decomposition, which suggested that a better comparison could be obtained by increasing the amount of simulant and keeping the time of reaction constant at 4 minutes. This approach was used in evaluating the last series of clays, RT001 through RT009, received from Anglo-American Clays Corporation.

A 200 mg sample of finely ground powder was treated with a measured (5-100 μL) amount of simulant and mixed in a vortex mixer for 1 minute (Section II.F). The mixture was allowed to stand for 4 minutes. Then 2 mL of diethyl ether was added and the powder extracted by vigorous stirring. The solid was separated by centrifugation and an aliquot of the ether analyzed by GC-AFID. A simulant solution of known concentration was used as the standard and the results were expressed as percent simulant remaining after 4 minutes.

(1)   CEES

Table IX and Figures 8 and 9 show the results obtained with the samples RT001 through RT009 with CEES. The decomposition of 20 μL of CEES was about 90% with sample RT004

and 75% with RT006. RT007 and RT009 were tested with 30 μL of CEES; however, the results suggest that they too would have given extensive decomposition with 20 μL. All of the clays were greatly superior to Fuller's Earth.

Longer reaction times gave more complete decomposition of the simulant. That was demonstrated with the 5 μL samples reported in Table III and was confirmed by observing that of 40 μL of CEES, only 44% and 36% remained after 30 minute exposure to RT004 and RT006, respectively. These clays gave 50% and 52% at 4 minutes.

The addition of CEES or DECP to RT008 caused the solid to develop a yellow color. Clay RT009 is grey and on addition of the simulants became deep black. It was clear that the two clays indicate the presence of these two simulants and could indicate the completion of the decomposition.

Both RT008 and RT009 have metal ions intercalated into the clay crystal lattice. The color changes suggest that metal-intercalated clays could be used for developing a solid which could detect contaminated areas and indicate when decomposition was complete.

Late in the last quarter of this contract, the Contract Officer's Technical Representative provided samples of polymer resins from Rohm and Haas for comparison with the clays received from Anglo-American Clays. These polymers were labeled A through F and were described as being mixtures of a strong acid resin, a strong base resin, and a carbonaceous adsorbent. These samples differed in the ratio of the three components.

The polymers of Rohm and Haas were studied in a similar manner to that for the clays. Except for Sample A, for which 64% of CEES remained, there was no apparent decomposition of 5 μL of CEES within 4 minutes. These results are given in Table XIV. It was clear that no appreciable reaction had occurred between CEES and polymers B through F. Polymer A showed less reactivity than the worst of the modified clays.

(2) DECP

The application of the 4 minute kinetic test with DECP proved to have a pitfall. Some of the powders treated with DECP were not wetted by the simulant; this factor probably slowed the reaction. Other powders formed balls around the simulant. Ball formation interfered with the interaction of more powder with the simulant and, of greater importance, interfered with extraction of the simulant by ether in the final

TABLE XIV

REACTIONS OF ROHM AND HAAS RESINS WITH CEES

Resin	Percentage of Agent Remaining After 4 Minutes Reaction with Increasing Volumes of Simulant		
	5 µL	10 µL	20 µL
A	64%	62%	75%
B	100		
C	100		
D	99		
E	99		
F	92		

analysis step. For example, in the test with clay RT009 only 4% of a 60 μL sample of DECP was extracted with ether. If the lumps were carefully broken during the extraction, about 80% of the DECP was recovered unchanged.

This observation may be highly significant, for if these powders were used as decontaminants, they might encapsulate G agents as they did the DECP. If a G agent were not extractable by ether in this condition, it would probably be ineffectual against a barrier composed of the powder. Thus a physical decontamination may have been achieved even though a complete chemical decomposition did not occur. The same effect was observed with RT004, RT006, and RT008, although to a much smaller extent. This encapsulation of simulant by RT009 occurred each time. The results of the 4 minute test with vigorous stirring of ether during extraction are given in Table XV.

The results of the test with Rohm and Haas polymers showed high percents of decomposition with samples A-D (Table XVI). The results with 10 μL were probably not due to the encapsulation effect observed with RT009 for a rerun of resin A with careful mixing gave 21% recovered DECP.

Summary

With the HD simulant CEES the modified clays were clearly superior to the polymers. The better clays were:

·RT004
·RT006
·RT007
·RT009

With the G-agent simulant DECP, RT009 showed an unusual property of encapsulating the simulant and preventing its extraction by ethe . For decomposition of the simulant, the polymers were probably superior to the clays, although the data do not rule out an encapsulation mechanism for polymer performance.

f)   Modified washer test

In tests of a plug of powder as barrier, the breakthrough time and the amount of simulant required for the breakthrough should indicate the combined adsorptive and reactive properties of the powder. Since the density, particle size, and degree of packing could vary in preparing the plug, a number of different techniques were used to develop a standard procedure.

In the first variation of the washer test (Section II.E), washers with outer diameter of 22.5 (±0.02) mm, inner

TABLE XV

DECOMPOSITION OF DECP BY CLAYS

Clay	Percentage of DECP Remaining After 4 Minutes Reaction with Increasing Volumes of Simulant						
	10 µL	20	30	40	60	80	100
RT006	61	68		77	79		
RT009			52		84	99	94

TABLE XVI

REACTION OF ROHM AND HAAS RESINS WITH DECP

Resin	Percentage of Agent Remaining After Reaction for 4 Minutes with Increasing Volumes of Simulant		
	10 μL	60 μL	100 μL
A	2.8	21	43
B	8.1	52	
C	4.6	30	67
D	0.9	61	
E	44	79	
F	71	85	

diameter of 9.7 (±0.02) mm, and thickness of 2.3 (±0.1) mm were
lightly packed by pressing the clay gently with a microscope
slide. The excess clay was removed by scraping the top of the
washer with the slide. The results of this test method with
RT001-RT006 and 4952-4955 are given in Tables XVII and XVIII.
With CEES the results were consistent and reasonably reproducible.
With DECP, however, some of the powders swelled and channeling
occurred. This led to erroneous results. Also the thickness
of the plugged washers gave long test times with the more
effective powders.

In an attempt to improve the test, a 5 mL
round-bottom flask was pressed into the clay plug to compress
the powder further and to indent the surface to form a well
for the simulant. Results with this method were difficult to
reproduce and erratic. With Fuller's Earth and some of the
resins, DECP did not penetrate because of its viscosity and
its failure to wet the powder. These results would be misleading,
for an effective decontaminant must wet the powder.

The best reproducibility with CEES was obtained
by a further modification. The washer, attached to M8 paper,
was packed with powder with pressure from a microscope slide
until excess powder was squeezed out over the sides of the washer.
The excess powder was removed by scraping the slide over the
washer. A 5 mL round-bottom flask was pressed tightly against
the inside rim of the washer. The weight of powder in the washer
was determined. Simulant was added (10 µL CEES or 20 µL DECP)
every 4 minutes until breakthrough was observed by a color change
in the M8 paper. The results obtained with CEES are given in
Tables X and XIX.

Since the amount of powder packed into the washer
by this method varied widely, a factor (µL simulant X time/mg
of powder) was calculated to normalize the data. Of the Anglo-
American Clays samples, RT004, RT008, and RT009 gave promising
results. With the Rohm and Haas polymers, Samples D and F gave
promising results. Unfortunately the highly promising Sample
F was not available in sufficient quantity to repeat the test.
In view of the results of the 4 minute kinetic evaluation this
value seemed questionable (see Tables XIV and XVI).

Values for DECP evaluation by the washer test
have not been included, since reproducible results were not
obtained. For example, one run of Fuller's Earth did not show
breakthrough even though no additional DECP could be added without
overflowing the washer. Similarly some of the clays and resins
formed solid layers on the surface of the washer which did not
seem to be penetrated by DECP. However, the color which developed
on M8 paper after liquid broke through RT004 and RT006 was neither

TABLE XVII

RESULTS OF WASHER TESTS ON CLAYS RECEIVED 8/84
USING CEES AS SIMULANT

Clay	Replicate	Interaction Time (min:sec)
RT001, Acid Activated (a)	1	11:00
	2	5:30
	3	11:00
RT002, Acid Activated (b)	1	10:30
	2	11:30
	3	10:00
RT003, Beneficiated	1	22:00
	2	17:00
	3	14:30
RT004, Beneficiated-Calcined	1	36:00
	2	39:00
	3	28:00
RT005, Al^{+3}/Cr^{+3} Intercalated	1	17:00
	2	15:00
	3	16:00
RT006, Cr^{+3} Intercalated	1	16:30
	2	14:00
	3	14:00
4953	1	32:30
	2	28:00
	3	18:00

TABLE XVIII

THE RESULTS OF THE WASHER TEST WITH MODIFIED CLAYS

Clay	CEES		DECP	
	Breakthrough Time Average of Three Determinations (min:sec)	Total Simulant Added (µL)	Breakthrough Time Average of Three Determinations (min:sec)	Total Simulant Added (µL)
Acid Wash, 4952	26:30	70	51:50	310
Acidified Surface, 4953	26:50	70	49:40	290
Al^{+3} cation intercalated, 4954	9:10	30	46:00*	270
Ethylene diamine treated 4955	23:50	60	43:35	250
Beneficiated, calcined, RT004	34:20	90		
Fuller's Earth	13:00	40	30:00	190

*The value for a single run since the replicate runs were invalid due to the failure of the pellets.

TABLE XIX

EVALUATION OF ROHM AND HAAS RESINS WITH TIGHTLY PACKED WASHERS USING CEES

Material	Wt (mg)	Breakthrough Time min:sec	Total Simulant μL	Simulant μL X sec/mg
A	76	0:51	10	9
	84	1:30	10	11
B	80	1:50	10	14
	75	4:29	20	36
	83	4:10	20	30
C	78	1:40	10	13
	85	1:16	10	9
D	68	6:02	20	106
	66	5:40	20	104
E	95	1:20	10	8
	79	0:33	10	4
F	52	12:35	40	580

that observed after breakthrough of the other clays and resins nor the color caused by DECP. This suggested that DECP had undergone reaction with these two clays and the material passing through was no longer DECP.

2. Attempts to Determine the Reaction Products

Acetone extraction RT004 after treatment with DECP showed only a small amount of DECP in the extract. An extract of the clay with deuterate dimethyl sulfoxide (DMSO-D_6) showed two ^{31}P signals in the phosphorus nuclear magnetic resonance (PNMR). One of these was due to unreacted DECP and the other signal was at a chemical shift expected for $(EtO)_2PO_2H$ or its anion.

A washer test was run with RT008 and DECP modified so that liquid on breakthrough was caught on a sodium chloride plate and the infrared (IR) spectrum was measured using the Fourier Transform Infrared. In the spectrum, shown in Figure 10, DECP is indicated by the background absorption and a large peak at 1035 cm^{-1}, which may be due to phosphate ion. Trisodium phosphate absorption is shown as a broad peak at 1015 cm^{-1}.[5] Many other species absorb in this region of the spectrum, however. The spectrum of the DECP used is given in Figure 11, showing absorption assignments.

Similar attempts were made to determine the material remaining on the clay powders after treatment with CEES. The ratio of CEES to clay RT004 was based on the data in Table IX to ensure the presence of some unchanged CEES. The mixture was extracted with ether to remove the excess CEES. After drying, the clay samples were extracted with D_6-DMSO. The proton nuclear magnetic resonance (^1HNMR) of the D_6-DMSO extract (Figure 12) shows water and ether as impurities in unchanged CEES (Figure 13).

These experiments suggested that CEES and DECP reacted with the oxygens of the clay by a nucleophilic mechanism. The products of these reactions, hydroxyethyl ethyl sulfide from CEES and diethylphosphate from DECP, were bound to the clay surface through a bond with oxygen. Since these hydrolysis products were bound to the clay, they were not extracted by the solvents used. With DECP the reaction may have been catalytic, so water present in the crystal lattice released diethylphosphoric acid, which was the first breakthrough product.
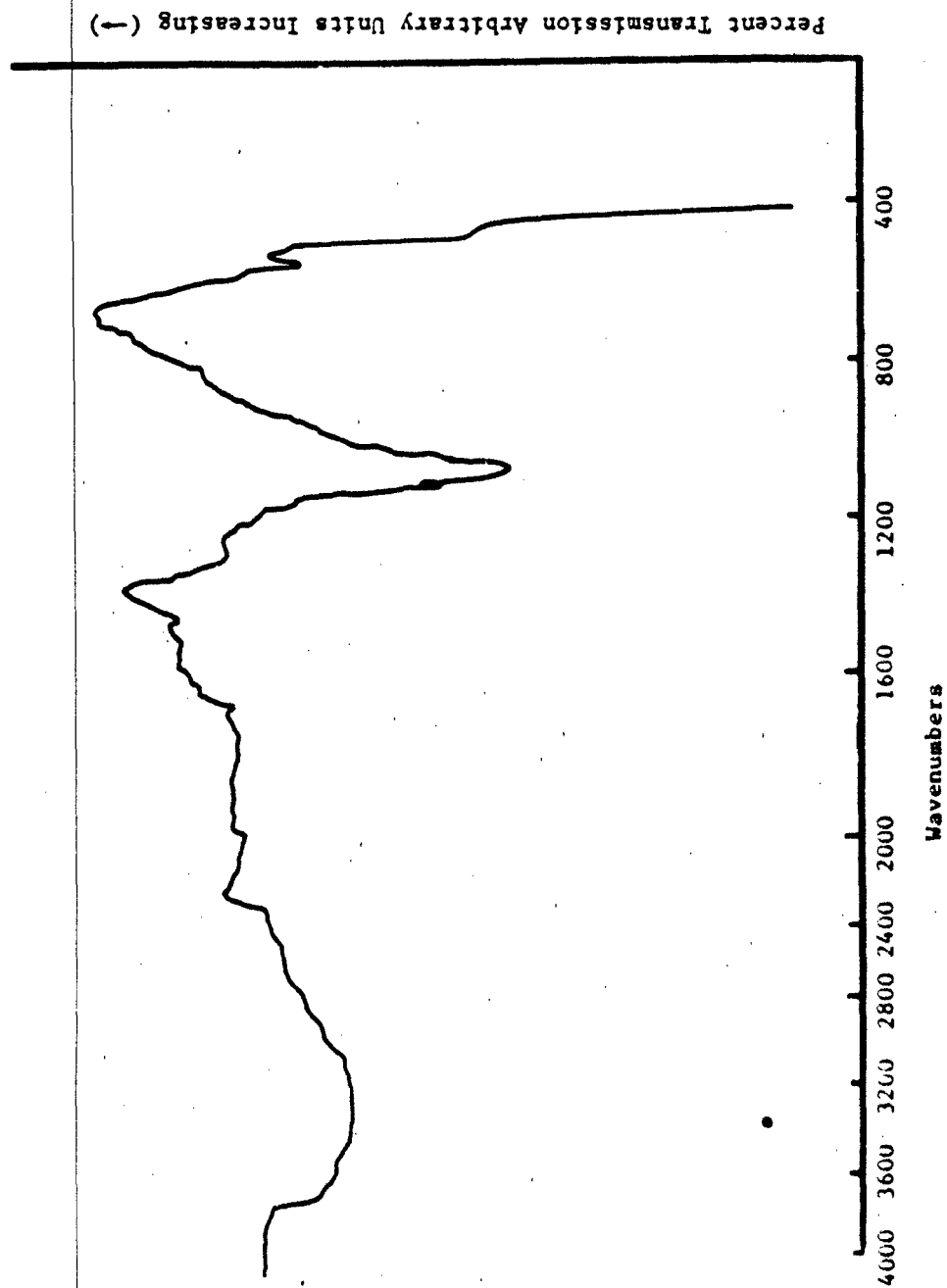
65

Percent Transmission Arbitrary Units Increasing (→)

Wavenumbers

Figure 10.   The Fourier Transform Infrared Spectrum of the Break-
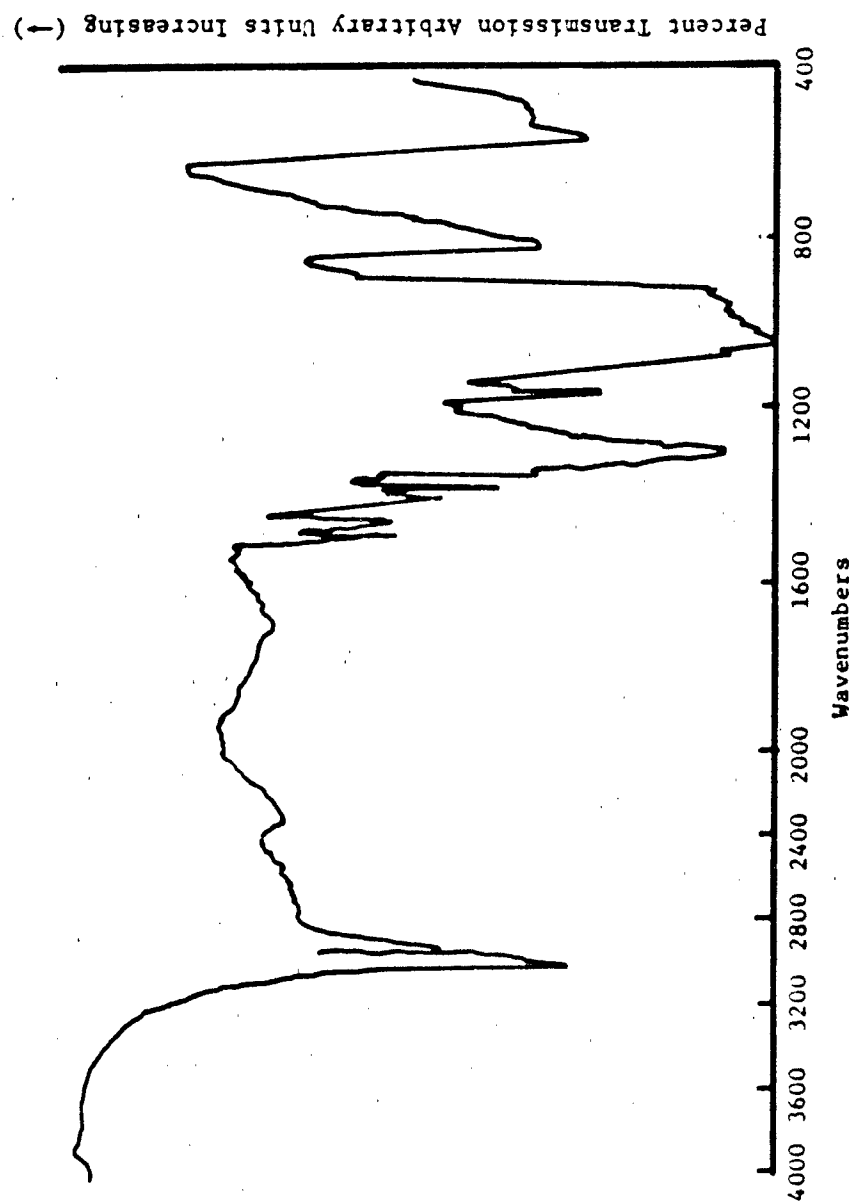through Product of DECP with Clay RT008.

66

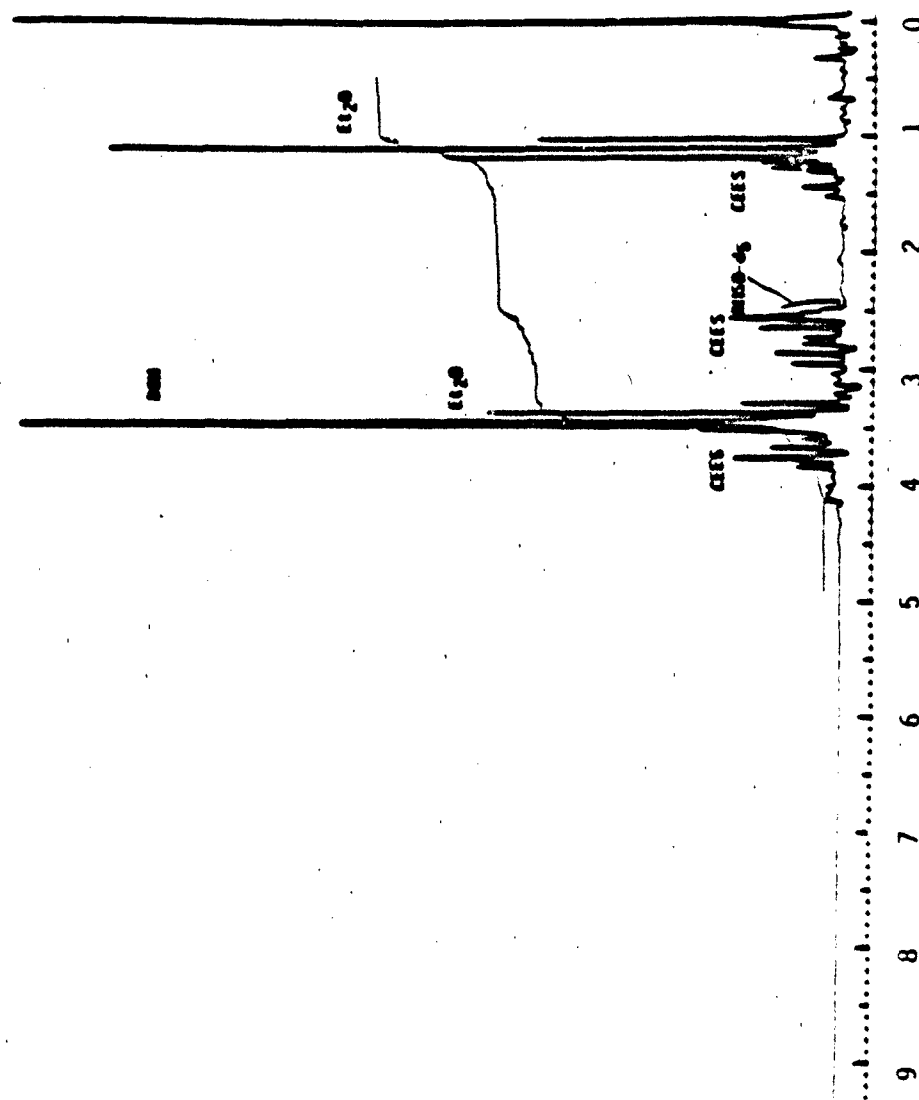Figure 11. The Fourier Transform Infrared Spectrum of DECP.

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Figure 12. ^{1}HNMR of the DMSO Extract of CEES After Treatment with Clay RT004.
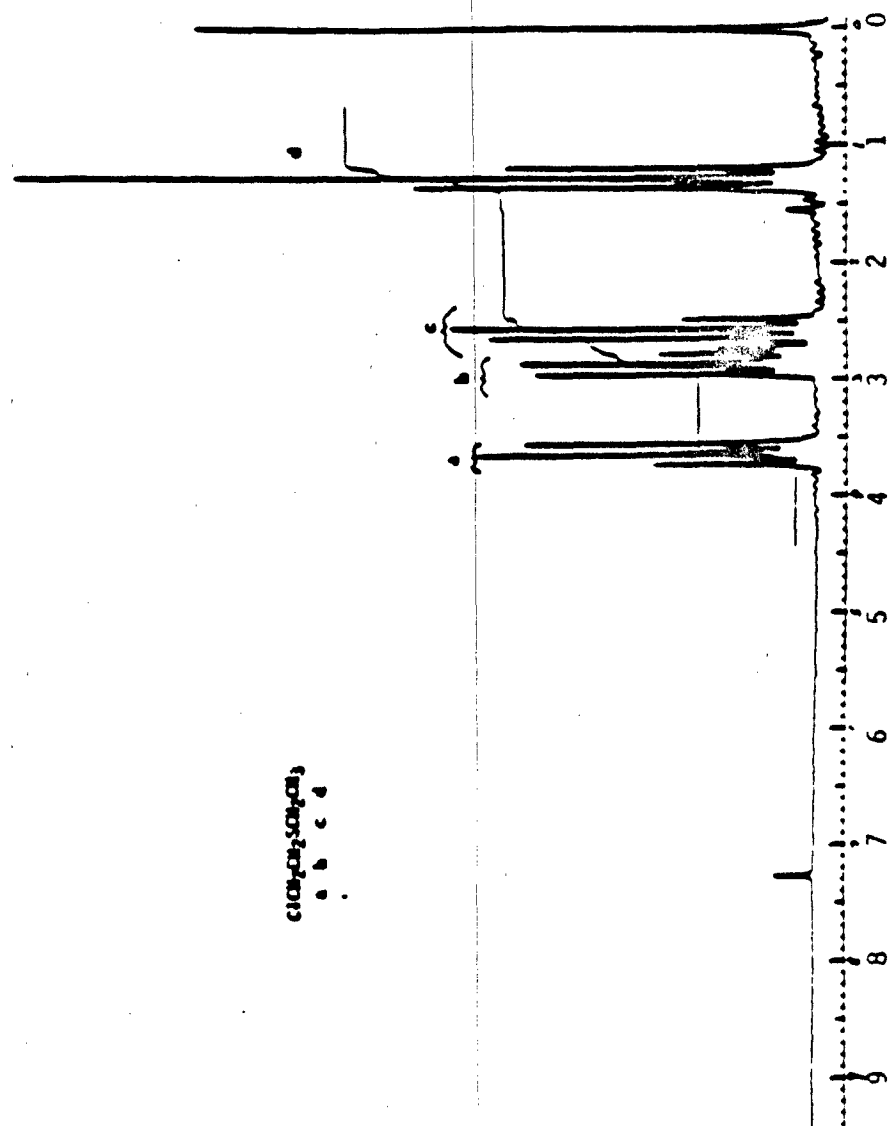
ClCH₂CH₂SCH₂CH₃
a b   c d

Figure 13. The ¹HNMR of CEES.

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D. Grafted Films

1. Preparation

The irradiation of polyethylene films in the presence of reactive vinyl groups was used to graft 2-vinylpyridine, 4-vinylpyridine, and 4-chloromethylstyrene onto the inert polymer film. These reactive functions were converted to quaternary salts by reaction of methyl iodide with pyridine and of trimethylamine with 4-chloromethylstyrene. The products of these reactions are illustrated in Diagram 1.

Films prepared by gamma-irradiation grafting of polyethylene with 2- (see A) or 4-vinylpyridine (see B) were treated with hydrobromic acid and bromine to give the hydrobromide perbromide. The chlorochromate salt was also formed. The parent films were converted to the methyl quaternary salts with methyl iodide or dimethyl sulfate (see C and D). By an ion exchange process, the quaternary salts of the two series were converted to the polyiodide, azide, hydroxide and thiosulfate.

Because of the problem of possible covalent bond formation between the nucleophiles and the grafted polymers with quaternized pyridine rings and the oxidization of the ring by oxidizing anions, a reactive polyethylene film was prepared from 4-chloromethylstyrene (see E). This film was then treated with trimethylamine or triethanolamine. The quaternary trimethylamine salt was formed, as shown by infrared spectral analysis, but triethanolamine did not form a salt. The quaternized film (BD-5-Q) was converted to the hydroxide, azide, perchlorate, chlorate, permanganate, dichromate, persulfate, perborate, m-chloroperbenzoate, and hypochlorite salts (structures given in Diagram 1 and Table XI). The structures of the films are shown in Diagram 1.

2. Evaluation

These films were evaluated using dibutyl sulfide or CEES as simulants for the blister agent HD. DNPP, paraoxon, was used as a simulant for G nerve agents and EEMPT was used as a simulant for the nerve agent VX. A summary of the results is given in Table XI.

The HD simulants were evaluated with representative examples of all of the films, as described in Experimental Methods. Using this procedure, the quaternary periodides and azides gave no reaction after several hours. The periodide was too poor an oxidizing agent to convert sulfides to sulfoxides. The azide was expected to cause the nucleophilic displacement of the halide of CEES. The lack of reactivity may have resulted from covalent bonding of the azide ion to pyridinium moiety, giving dihydropyridines which were no longer nucleophilic (see Equation 1). The blue color of the film was also consistent with this hypothesis.
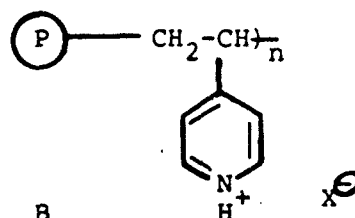
70

DIAGRAM 1
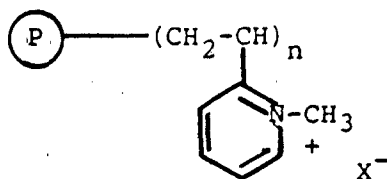
STRUCTURE OF THE REACTIVE FILMS
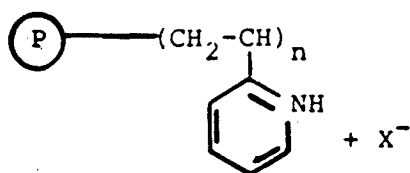
A

BD-1-HBr$_3$, X=Br$_3^-$
BD-1-HCrO$_3$Cl, X=CrO$_3$Cl$^-$

B

BD-2-HBr$_3$, X=Br$_3^-$
BD-2-HCrO$_3$Cl, X=CrO$_3$Cl$^-$

C

BD-1-QI$_3$, X=I$_3^-$
BD-1-QOH, X=OH$^-$
BD-1-QS$_2$O$_3$, X=S$_2$O$_3^=$
BD-1-QN$_3$, X=N$_3$
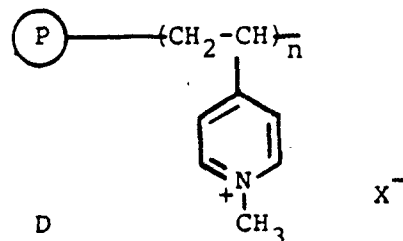
D

BD-2-QI$_3$, X=I$_3^-$
BD-2-QS$_2$O$_3$, X=S$_2$O$_3^=$
BD-2-QN$_3$, X=N$_3^=$
Copolymer with divinylbenzene
BD-3-QOH, X=OH$^-$

E

$\xrightarrow{\text{Me}_3\text{N}}$
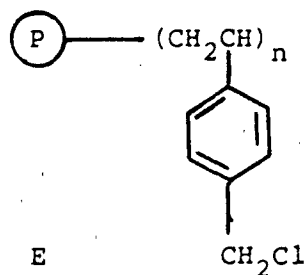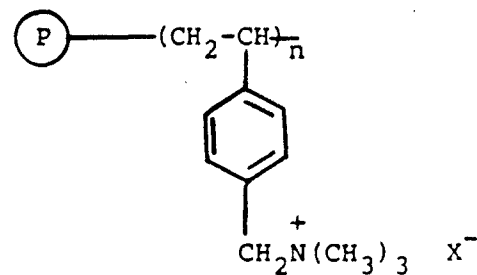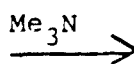
BD-5-QX, X$^-$
X=N$_3^-$, OH$^-$, ClO$_4^-$, ClO$_3^-$
MnO$_4^-$, Cr$_2$O$_7^=$, SO$_5^=$,
m-ClC$_6$H$_4$CO$_3^-$, ClO$^-$

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Equation 1

BD-2-Q-N$_3$
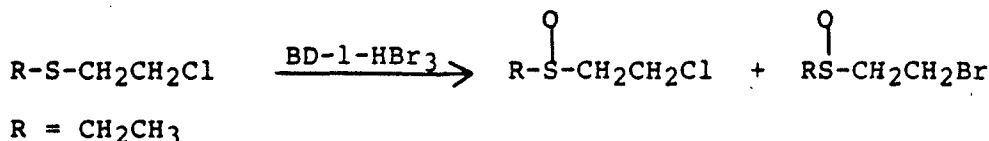
covalent
bond
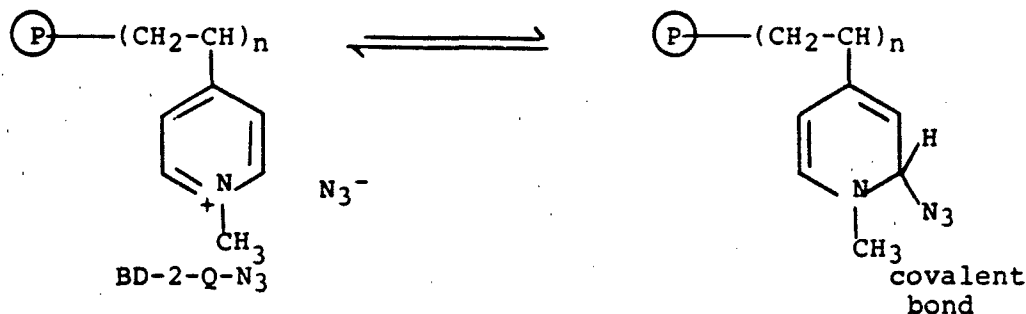
The hydrobromide perbromide forms of the films, prepared from polyethylene grafted with 2- and 4-vinylpyridine, were a reddish-brown color. Any reaction which resulted in reduction of the perbromide was accompanied by loss of this color. The reaction of either film with dibutyl sulfide or CEES caused an immediate color loss at the site of contact, and analysis of the product showed the formation of the sulfoxide corresponding to the sulfide used. With CEES nucleophilic displacement of Cl$^-$ by Br$^-$ also occurred (see Equation 2).

Equation 2

$$R-S-CH_2CH_2Cl \xrightarrow{\text{BD-1-HBr}_3} R-\overset{\displaystyle O}{\underset{\displaystyle \|}{S}}-CH_2CH_2Cl \ + \ R\overset{\displaystyle O}{\underset{\displaystyle \|}{S}}-CH_2CH_2Br$$

R = CH$_2$CH$_3$

Since the simulants were used neat, the reaction rapidly depleted the available perbromide at the site of contact on the film. Reaction continued at a rate controlled by the diffusion of the simulant through the film. The film became transparent and colorless as the perbromide was depleted. The rate of the reaction could be followed by measuring the area of the colorless spot. The principal product of the reaction, even after several hours, was the sulfoxide corresponding to the sulfide used.

The perbromide films BD-1-HBr$_3$ and BD-2-HBr$_3$ gave a faint odor of bromine. The stability of the films was determined by allowing them to stand and then reevaluating their reactivity. Even after 7 days, BD-2-HBr$_3$ still converted sulfide to the sulfoxide. These films gave no reaction with the simulants DECP, DNPP or EEMPT.

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Samples of the hydrobromide perbromide of the 2- and 4-vinylpyridine-grafted films (BD-1-HBr$_3$ and BD-2-HBr$_3$, respectively) were given to the COTR of this project for evaluation of detoxification of surety chemical agents.

The success with grafted oxidizing agent perbromide suggested the testing of other oxidizing films. The chlorochromate form was prepared from the 2- and 4-vinylpyridine films to give BD-1-HCrO$_3$HCl and BD-2-HCrO$_3$Cl. Neither of these films reacted with the sulfides.

The quaternary hydroxide BD-1-Q-OH gave a very slow reaction with DNPP (Table XII). BD-3-Q-OH, prepared from the 4-vinylpyridine quaternary salt, reacted rapidly with DNPP, as did hydroxide ion.

The difference in reactivity of the quaternary hydroxides BD-1-Q-OH and BD-3-Q-OH (see Table XII) may reflect the difference between covalent bond formation with 2- and 4-pyridinium hydroxide (Equation 3). In view of this possibility, the film BD-5-Q was converted to the hydroxide form, since the trimethylammonium hydroxide could not form a covalent bond. This benzyl film BD-5-Q-OH reacted with all the simulants (see Table XI).

Equation 3
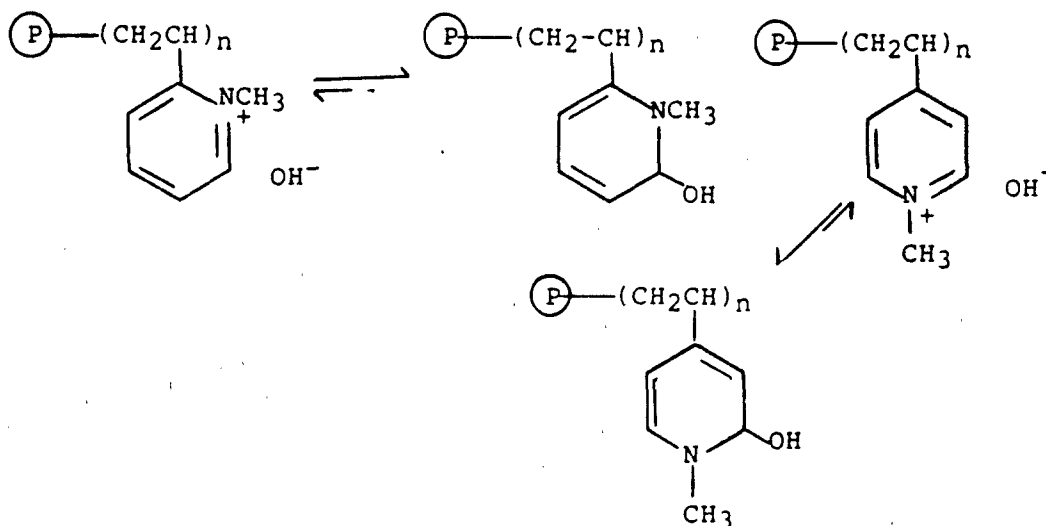
A film with a good nucleophile was prepared by exchanging chloride ion with thiosulfate to give BD-2-Q-S$_2$O$_3$. On reaction with CEES, the peak in the GC for the HD simulant disappeared

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and no new signal was evident. This observation was consistent with a nucleophilic displacement of the chloride ion by thiosulfate, the product of which would be non-volatile and associated with the film.

The most reactive film with a solution of DNPP was the thiosulfate form (BD-2-Q-S_2O_3). The reaction was evaluated by the change in ultraviolet absorption (Table XII). The details of the evaluation procedure are given in Experimental Methods. The disappearance of ultraviolet absorption for the simulant was very rapid; however, the nature of the product was in question. Hydrolysis of the simulant would give the p-nitrophenolate ion, which is a deep yellow. This was observed with BD-3-Q-OH. However, addition of hydroxide to the BD-2-Q-S_2O_3 film after reaction with DNPP did not give a yellow color. Thus another nerve agent simulant must be used with this thiosulfate film. The V simulant EEMPT did not react with this film.

A preliminary, qualitative test of BD-1-HBr_3 and BD-2-HBr_3 with EEMPT gave no color change with the films.

The BD-5-Q films with oxidizing anions were surprisingly inert. The perchlorate, chlorate, permanganate, dichromate, peroxyacid, and hypochlorite did not react with EEMPT and reacted with DECP only if the film was moist. The colored films from permanganate and dichromate gave no change on treatment with CEES; however, there was a decrease in the GC peak for CEES, EEMPT, and DECP when the hypochlorite or peroxyacid films were wetted and then treated with CEES (Tables XX, XXI and XXII).

3.   Detector Films

Several of the films were colorless because of the anion present. Thus the films containing periodide, perbromide, chlorochromate, permanganate, dichromate, and pyridinium azide each had a detectable color which changed on reaction of the anion with a simulant or other agent. Unfortunately these films did not have the best reactivity with the simulants of chemical agents. The more reactive films were BD-5-Q-OH, BD-5-Q-N_3, and BD-2-Q-S_2O_3, all of which were lightly colored or colorless.

It was therefore desirable to add a dye or indicator to the more reactive films to provide a mechanism for monitoring the reaction by a color change. Since these films were all nucleophilic in reactivity, acid-base indicators were appropriate for detecting reactivity with the nucleophilic anion. After washing the grafted films in the appropriate solution of the indicator dye, reaction of the films with simulants gave color changes, as indicated in Table XXIII.

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TABLE XX

REACTION OF GRAFTED FILMS WITH CEES

| Film | Percent CEES Remaining Time (minutes) | | | | | | Method* |
	1	5	10	20	40	60	
BD-5-Q treated with m-Chloroperoxybenzoate							
Batch #1 ((from Cl⁻))	No Reaction						A
Batch #3 ((from OH⁻))	No Reaction						A
BD-5-Q BO_3^-	No Reaction						A
BD-5-Q $S_2O_8^{--}$	--	87	82	77	--	--	A
BD-3-Q OCl^-	84,94	--	--	--	--	--	A
BD-3-Q OCl^- (saturated with water)	--	66,67	--	--	--	--	A
"	86	75	69	61	59	53	B
BD-3-Q OCl^- (air dried)	88	87	81	71	68	65	B
BD-3-Q OCl^- (saturated with water)	88	81	78	60	64	54	A
BD-3-Q OCl^- (treated with: n-butylsulfone	No Reaction						B
tetramethylene sulfone	No Reaction						B
S-84A ($SOCl_2$, DETA)	93	88	86	88	88	85	B
BD-5 (treated with neat DETA on steam bath 68 hr, then 5% NaOH in water)	91	88	83	86	84	86	B

*Method A - 1 µL neat simulant spiked onto film

Method B - 5 µL of a 20% solution of simulant in diethyl ether spiked onto film

TABLE XXI

REACTION OF GRAFTED FILMS WITH EEMPT

Percent EEMPT Remaining

Film	Time (minutes)			Method*
	5	10	20	
BD-5-Q treated with m-Chloroperoxybenzoate				
Batch #1 (from Cl⁻)	84	71	62	A
	93	83	88	A
Batch #3 (from OH⁻)	No Reaction			
BD-5-Q BO$_3^-$	77	84	82	A
BD-5-Q S$_2$O$_8^{--}$	87	83	83	A
BD-3-Q OCl⁻	2 Replicates at t = 1 min 92, 97%			
BD-3-Q OCl⁻ (saturated with water)	2 Replicates at t = 5 min			A
"	No Reaction for 60 min kinetic run			A
S-84A (SOCl$_2$, DETA)	No Reaction for 60 min kinetic run			A
BD-5 (treated with neat DETA steam bath 68 hr, then 5% NaOH in water)	No Reaction for 60 min kinetic run			A

*Method A - 1 µL neat simulant spiked onto film

TABLE XXII

REACTION OF GRAFTED FILMS WITH DECP

Film	Percent DECP Remaining Time (minutes)						Method*
	1	5	10	20	40	60	
BD-5-Q treated with m-Chloroperoxybenzoate							
Batch #1 (from Cl⁻)	--	50	28	13	--	--	B
	--	47	28	14	--	--	B
Batch #3 (from OH⁻)	--	27	7	2	--	--	B
Batch #3 (treated with water)	--	19	7	2	--	--	B
BD-5-Q BO₃⁻	--	42	17	1	--	--	B
BD-5-Q S₂O₈⁻⁻	--	93	85	73	--	--	B
BD-3-Q OCl⁻	91,93	83,83	--	--	--	--	B
BD-3-Q OCl⁻ (saturated with water)	--	38,47	22,31	--	--	--	B
S-84A (SOCl₂ DETA)	78	31	17	7	0	0	B
BD-5 (treated with neat DETA on steam bath 68 hr, then 5% NaOH in water)	82	56	10	5	0	0	B

*Method A - 1 µL neat simulant spiked onto film

Method B - 5 µL of a 20% solution of simulant in diethyl ether spiked onto film

TABLE XXIII

COLOR REACTIONS OF INDICATOR FILMS WITH SIMULANTS

Indicator	BD-5-QNMe₃OH Film	DECP	CEES
a) Bromothymol blue	Dark Blue	Green-Yellow	Dark Blue
b) Cresol Red	Dark Red	Lightened Orange	Red
c) Bromocresol green-Methyl red	Dark Green	Yellow	Dark Green
d) Dibromo-o-cresol sulfonaphthalein	Dark Purple	Yellow	Dark Purple
e) 4,5-Dihydroxy-3(p-sulfophenyl azo-2,7-naphthalene disulfonic acid trisodium salt	Dark Red	Red	Dark Red
f) Janus green B	Colorless		
g) Potamine fast green GL	Green	Green	Green
h) Potamine green 26B	Dark Green	Dark Green	Dark Green
i) HACH wide range H indicator	Green	Orange	Green
j) Phenolphthalein	Pink	Colorless	

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TABLE XXIII. (cont.)

Indicator	BD-5-QNMe$_3$S$_2$O$_3$ Film	DECP	CEES
a)	Green	Yellow	Green
b)	Yellow	Orange	Yellow
c)	Light Blue	Colorless	Light Blue
d)	Dark Blue	Green-Yellow	Dark Blue
e)	Violet	Violet	Violet
f)	Colorless		
g)	Colorless		
h)	Light Green	Light Green	Light Green
i)	Blue	Lightened Yellow	Blue

E.   Polymeric DS-2 Analogs

   1.   Films with Grafted DS-2

      The nucleophilic films evaluated previously showed little or no reactivity with the simulant for HD. Since DS-2 (a sodium hydroxide-containing decontaminant) is highly effective for deactivation of HD, the grafting of DETA onto the film would be expected to improve its reactivity.

      Polyethylene film grafted with vinylbenzylchloride should provide the starting material for introducing the DETA moiety. However, no reaction of neat or diluted (aqueous) amine with the benzylchloride function occurred. Only after heating the benzylchloride film with neat DETA for 65 hours was a significant amount of the amine introduced onto the film. A nonpolar solvent such as toluene assisted the reaction; however, the film disintegrated at high temperature. At room temperature DETA in toluene was introduced in only 24 hours.

   2.   Polymers with DETA Side Chains

      Since reaction of the benzylchloride group on the films proved difficult, a better approach seemed to be to prepare a poly DETA styrene to obtain the maximum density of reactive sites.

      The preparation of the polymer has been attempted by two different routes. 4-Chloromethylstyrene was treated with DETA to introduce the DETA side chain on the monomer, which was then polymerized. The second approach involved the conversion of chloromethylated polystyrene, prepared by polymerization of 4-chloromethylstyrene or by chlormethylation of polystyrene (Bio-Rad), to the DETA polystyrene by reaction with DETA.

      The chloromethylated polystyrene from Bio-Rad had about 64% of the phenyl rings substituted. Reaction of the polymer with DETA in toluene gave complete substitution of chlorine atoms. Thus this polymer had nearly the theoretical maximum number of DETA units.

      The polymerization of 4-chloromethylstyrene was accomplished by benzoyl peroxide catalysis to give 80% yield of a white solid polymer, which was soluble in methylene chloride and insoluble in methanol. A solution of the polymer in methylene chloride was treated with 2 molar equivalents of DETA. The mixture jelled within 15 minutes. More methylene dichloride was added; after stirring for 3 days, water was added to remove the DETA hydrochloride. The remaining solid was the polymer

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containing a DETA side chain. The polymer was insoluble in methanol, DMSO, acetone and acid.

A similar polymer was prepared by treatment of 4-chloromethylstyrene with DETA to form N-(4-vinylbenzyl)DETA. The ^{1}HNMR spectrum showed that the central or secondary amino nitrogen had undergone reaction, for the product seemed to be symmetrical.

The polymerization of monomer with DETA side chain was not easily accomplished. Radical polymerization using a peroxide catalyst was not successful, since the amine of the side chain acted as a chain stopper. Polymerization with hydrochloric acid was slow and gave low molecular weight polymer.

The N-(4-vinylbenzyl)DETA was successfully polymerized with 2,2'-azobis[2-methylpropionitrile] as initiator. The polymer was less rigid than that formed from chloromethylstyrene, indicating a lower molecular weight. Otherwise the polymers were very similar.

The treatment of either of the polymers having DETA side chains with Methyl Cellosolve caused the polymer to swell and absorb about 3.5 times its weight of solvent. A 20 g sample of polymer treated with a saturated solution of sodium hydroxide in Methyl Cellosolve (14.9%) gave 72 g of swollen polymer containing about 1.1% of sodium hydroxide, based on sodium ion analysis.

A series of solid mixtures of DETA polymer Methyl Cellosolve and sodium (potassium) hydroxide were reacted with CEES in the kinetic 4 minute test. The results showed more than 80% recovered simulant. With greater amounts of solid, CEES decomposition was only slightly increased.

This lack of reactivity probably reflects protection of the reactive amino side chain by the polymer chain. The swelling of the polymer by the adsorbed Methyl Cellosolve should provide a mechanism for the simulant and hydroxide to interact; however, because of the high concentration of Methyl Cellosolve, the mixture may not function as does DS-2. We will attempt to remove some of the Methyl Cellosolve so that the relative amounts of DETA side chain, hydroxide ion, and Methyl Cellosolve more nearly resemble those in DS-2.

IV. FUTURE WORK

The evaluation of the modified clays using simulants of nerve agents and mustards has been successful using the washer test and the 4 minute kinetic test. Similar investigations using the corresponding chemical surety agents would indicate whether the simulants are satisfactory and would help to determine the validity of the test procedures.

The decomposition of simulants by the modified clays studied appears to have a limit, which may suggest that the reaction is not catalytic. Improvement of the modified clays should be attempted by intercalation of metal ions to produce catalytic decomposition. New modifications should be evaluated when they are prepared.

Other variations producing expansion of the clay crystal lattice should also improve the reactivity of these clays. These modifications should also be studied in any future work.

It should be possible to duplicate the unique properties of DS-2 in a polymer system. The preliminary studies were not successful because too much Methyl Cellosolve was absorbed by the polymer. Future studies should attempt to match the proportions of DS-2 solution. This polymer, if shown to have high decontamination potentials, should be prepared in the form of nonwoven fabric, foam, and powder.

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